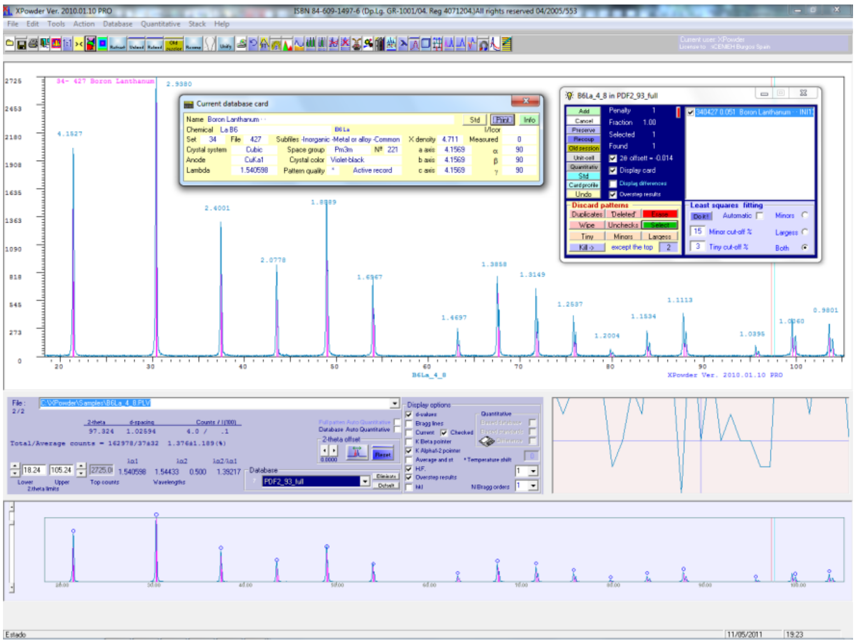
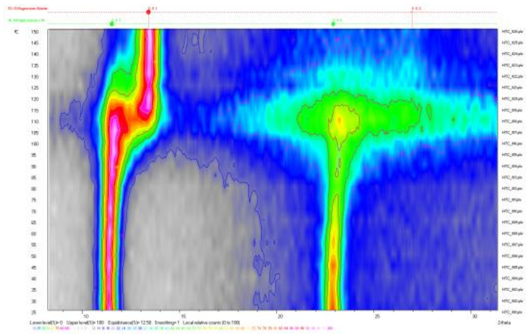
XPowder ™ XPowder12

A SOFTWARE PACKAGE FOR POWDER X-RAY DIFFRACTION ANALYSIS

User guide Ver 2004.04.82 | **Updates** | **New features** Ver 2010.01.10 | **Xpowder12** Ver 2012.02.01/04/22

Qualitative, quantitative and microtexture





The program uses PDF2 , AMSCD or customized databases

J. D. Martin (2008)

http://www.xpowder.com/
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XPowder

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User guide
Version 2004.04.82

XPowder12

XPowder12. New features

Qualitative, quantitative and microtexture

This manual is available in www.xpowder.com/ User guide
and can be freely copied and distributed

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Introduction

XPowder is a widely used program (Figures 1 and 2) that was created for the operating system Windows^{TM}, to facilitate the analysis of Powder X-ray diffraction patterns.

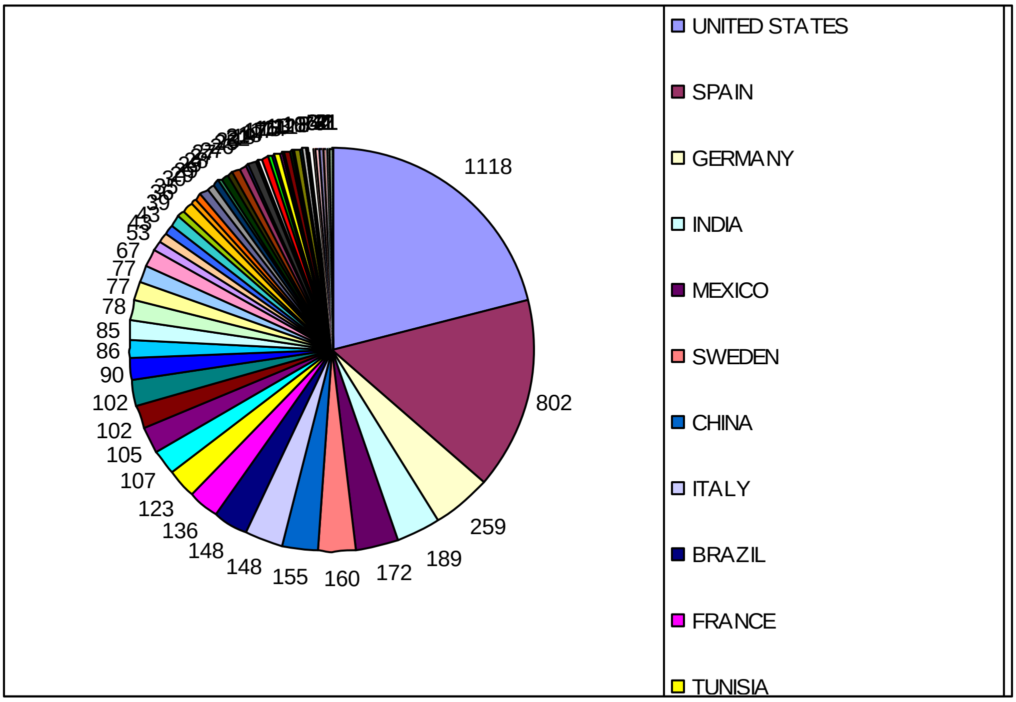


Figure 1. Number of downloads of the program XPowder from www.xpowder.com between January and September 2008 . The data are from 'Advanced Web Statistics 6.6' (build 1887) - Created by AWStats (GNU General Public License) and do not include downloads from unknown or repeated IP addresses.

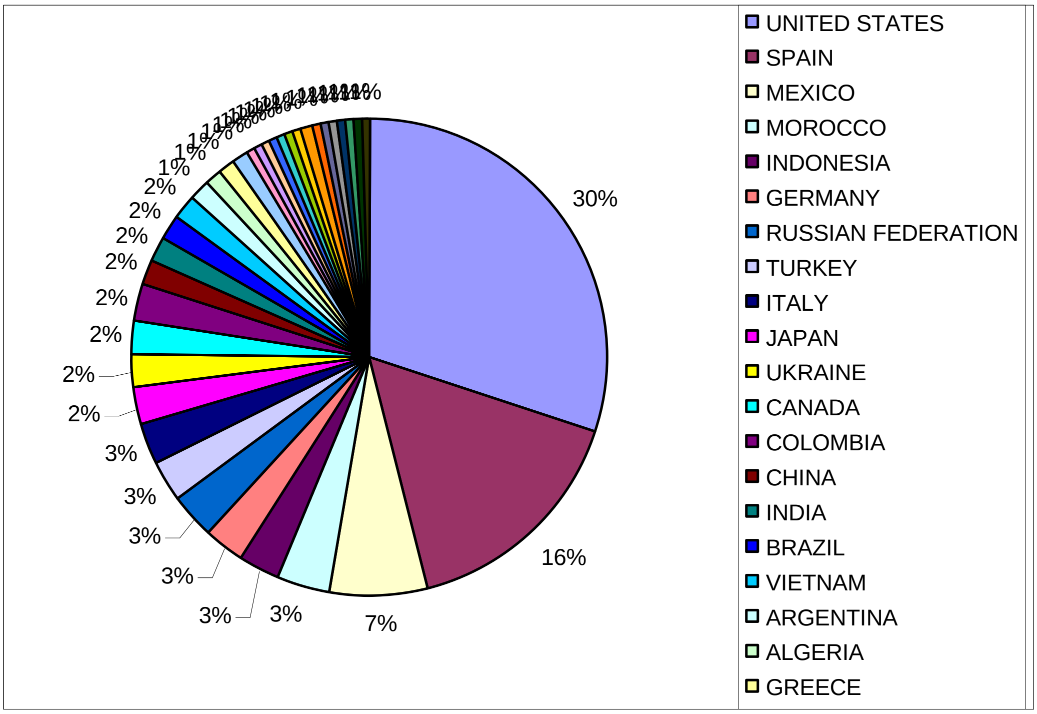


Figure 2. Geographic distribution in % of downloads of the program XPowder in the first half of October 2008, which corresponds to the start of the academic year 2008-2009.

This program recognizes files from most diffractometers, and handles a number of simple ASCII formats that can easily be generated for import. XPowder also lets you acquire data directly from some older diffractometers who did not have proper digital control for Windows operating system. Automatic sample-changer and monitoring of temperatures, are also handled by XPowder.

Files may contain data in the form of a list of intensities (counts, cps, absolute or relative intensities, etc.) from an initial angle 2θ, and constant $\Delta 2\theta^o$ step in a txt formats.

XPowder can also read 2D images (jpg, tiff, bmp, mccd, etc) obtained by instruments with CCD detectors and directly calculate their powder diffractograms.

Recognition of data formats.

* RAW	Binary. Siemens – Bruker diffractometers (1 to 4 versions)
* X'Pert	Html. Philips diffractometers
* RD	Binary. Philips diffractometers
* UDF	ASCII. Philips diffractometers
* CCD	All type of file images: jpg, bmp, etc. TERRA Diffractometers have a specific modulus.
* Ascii	2θ [separator] Intensidty (.txt, .asc, .xy)
* POW	
* GSAS	
* DBWS	
* DAT	
* UXD	Several kinds
* GRF	Cerius program calculated diffractograms
* Xye	Mercury program calculated diffractograms
* Sietronic cpi	
* Seifer nja	
* Etc.	

The program will recognize additional file formats in future versions. Please contact the author to request the inclusion of any specific format.

The conversion of any data file into one of the formats recognizable by **XPowder** is usually straight forward: PLV, the native format of XPowder (P,L and V are the consonants in *polvo* -powder in Spanish) is an ASCII text format with a very simple configuration containing the following information:

* First line: Information about the specimen.
* Second line: Starting 2θ angle at the beginning of the experiment.
* Third line: 2θ step between successive intensity measurements.
* Fourth line: $K\alpha_1$ wavelength in Å. The precision of the value in this line is not important since **XPowder** normalizes all the $K\alpha_1$, $K\alpha_2$ and $K\beta$ values according to the content of 'xpowder.ini' file.
* Fifth line to end: Experimental diffracted intensities (one per line).

An example of PLV file is given below:

```
RENDIJA=AUTOMATICA. CALCITA. Intensidad máxima:  10732.
3.00
0.06
1.54051
1
3
7
...
```

Other richer PLV formats (versions 2 and 3) contain additional information about the experimental conditions. The example below shows a PLV version 3 file.

```
XPowder diffraction software. PLV file format Ver. 3.0
Sample= Fluorita0.PLV
Site= Universidad de Granada (Spain)
User= Crista-Mine-Gr
Date= 18/06/2004
Time= 13:32:38
Start 2-theta scan= 3.000
End 2-theta scan= 80.000
Step size= 0.040
Scan mode= Continuous
Integration time(sec)= 0.4
Anode= Cu
Filter= None
Monochromator= Graphite 2°
K-Alpha 1=  1.54051
K-Alpha 2=  1.54433
Ka2/Ka1 Ratio=  0.5
K-Beta=  1.39217
Automatic sampler changer= NO
Single Gobel mirror= NO
Divergence slit= AUTOMATIC
Receiving slit= 1/0.1/1
Generator voltage(Kv)= 40.00
Tube currrent(mA)= 40.00
Maximun counts=  5194
Line   26
Line   27
Line   28
Line   29
Line   30
Line   31
Line   32
Temperature = 22
Line   34
Line   35
Line   36
Line   37
Line   38
Line   39
Line   40
Line   41
Line   42
Line   43
Line   44
Line   45
Line   46
Line   47
Line   48
Line   49
Data
   3.000        22
   3.040        20
   3.080        19
   3.120        15
   3.160        16
   3.200        21
   3.240        20
```

This file type uses' keywords' (*Start 2-theta scan* for example) followed by the sign '=' and the value of each argument (= *3.000*). The lines that contain the keyword '*Line*' are ignored by the program. From the keyword '*Data*' are tabulated values of '2θ' and 'intensities'. It can contain any number of lines of header and the order is irrelevant, except that the first line should contain the key *'PLV file format View. 3.0*' or ' *View PLV file format. 2.0* '. Version 2.0 is equal to 3.0 except that the data list can only contain intensity values (no 2θ angle).

What can you do XPowder?.

The main operations, as described in the following five points, are made by pressing buttons or selecting from pull-down or contextual menus. The latter appear when right-clicking the mouse on the graphic or object of interest:

1. Identification of crystalline compounds (Search-Match). It is necessary to have a database, such as' PDF2.DAT 'of the ICDD (International Center for Diffraction Data) and, or, the' Difdata.txt 'of AMSCD. The latter only contains minerals.

   The phase identification of samples with one, two or three major components is usually done with a single 'Click'. With more complex samples, either with more phases or minor components, the complete identification is achieved easily by using various tools such as subtraction of patterns already identified. All these tools are detailed in Chapters 2, 4 and 5.

2. Quantification of compounds. The quantification is done on full profile of the experimental diffractogram by non-linear least squares regression based on parameters such as 2θ displacement and profile function (Gauss, Cauchy, Pseudo Voigt, Pearson VII and asymmetry). All calculations are accompanied by statistics. The reference data for each phase can either be full patterns (experimental or calculated) or database records (positions and relative intensities). When using a **2θ/Ir** database, a Reference Intensity Ratio (RIR) must be used for each phase, and can manually entered if not provided in the database, or if particular experimental conditions require their adjustment. The calculation takes into account the absorption correction based on the chemical composition provided by the database. It also takes into account a parameter that represents an approximate percentage of amorphous phase in the sample. The program is designed to automatically carry out up to fifty simultaneous quantitative analyses. The results are presented in tabular form within the '*log file*' of each session. The quantification of compounds is detailed in chapters 6 and 7.

3. Crystal size, 'strain', thermal expansion tensor. Tools are provided for crystal sizes and 'strain' calculations using the 'Williamson-Hall' and 'Warren-Averbach' methods, in addition to the classic 'Scherrer' method. A specific tool allows calculating 'log-normal' distribution in very low crystallinity materials. This is detailed in Chapter 10. If the diffractogram records are made with temperature control, the thermal tensor can also be calculated (Figure 8.9).

4. Assorted tools.

   a. Automatic unit-cell refinement of identified phases (Chapter 9).
   b. "$K\alpha_2$ *stripping*" by a highly optimized Rachinger method.
   c. Automatic background subtraction. Smoothing (elimination of excessive vibrations and noise) by Fourier transform and functional filters.
   d. Calculation of powder diffractogram from electron or X-ray diffraction 2D images.
   e. Calculation of the diffractometer instrumental profile.
   f. Calculation of the Caglioti equation for real samples (Chapter 11).
   g. Calculation function of profiles and theoretical mixing patterns.
   h. Addition and subtraction of diffractograms.
   i. 2θ offset correction using standard pattern or harmonic peaks (Chapter 3).
   j. Logarithmic/Arithmetic scaling.
   k. Calculation of reciprocal histograms.
   l. Reporting text ('log file').

5. Graphic tools.
   a. Zoom.
   b. Choice of color palette and active diffractogram.
   c. Copy and paste images.
   d. Generation of graphics (bitmaps) and vectorial (hpgl) files.
   e. Dynamic 3-D representation of up to fifty patterns.
   f. 2D representation of diffractogram series (diffraction maps) with calculation of curves and level, or false color very useful for studies of phase changes and crystallinity (Chapter 8).

XPowder Installation

A single installation file (' *xpowder_setup.exe* ') is used for all program options (Trials, Academic, Professional, PLUS, etc.). It is available from www.xpowder.com (download) and can be freely copied or distributed.

Instructions:

1. Download the latest file version (2004.04.xx) of *xpowder_setup.exe* from www.xpowder.com

2. Double click on then *XPowder_setup.exe* installation icon.

3. Follow the instructions that will appear on the screen (figure 3).

4. If you have the license code of the program, insert it (preferable copy/paste) into the box

Main menu -> Help -> XPowder registration code

Please, backup this registration code because it is valid for future installations and/or updates. The XPowder program will be licensed and may be updated without having to re-input the code (this code is recorded in the text file 'Folder program / Code.txt'). If this file is deleted, the program will behave as a 'trial version' valid for 20 days, for analysis of up to 500 diffractograms.

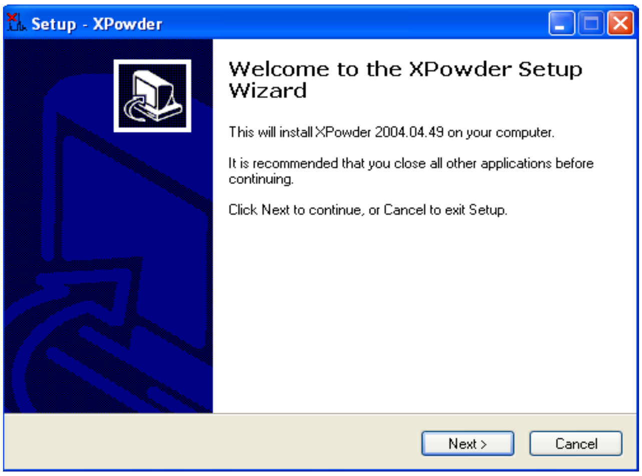


Figure 3

Database installation

The databases are not attached to the program and must be purchased separately. The databases recognized by XPowder 'PDF2.DAT' (between 500MB and 550MB or so, depending on the version) and 'DifData.txt' (approximately 65 MB). You can install both in parallel from the main menu:

Database-> Database install (or Database Update)

Select database file and then pulse Install (figure 4).

Database files could be:

- ICDD: 'PDF2.dat'
- AMCSD: 'cifdata.txt' (optional) + 'difdata.txt' (required). In any case, 'cifdata.txt' must be installed before the 'DifData.txt'. 'cifdata.txt' (approximately 31 MB) is an auxiliary file of 'difdata.txt', its use is optional and it can be deleted once the setup has been completed.

It is desirable that the databases are on your hard drive rather than on a CD-ROM or DVD in order to optimize the searching speed.

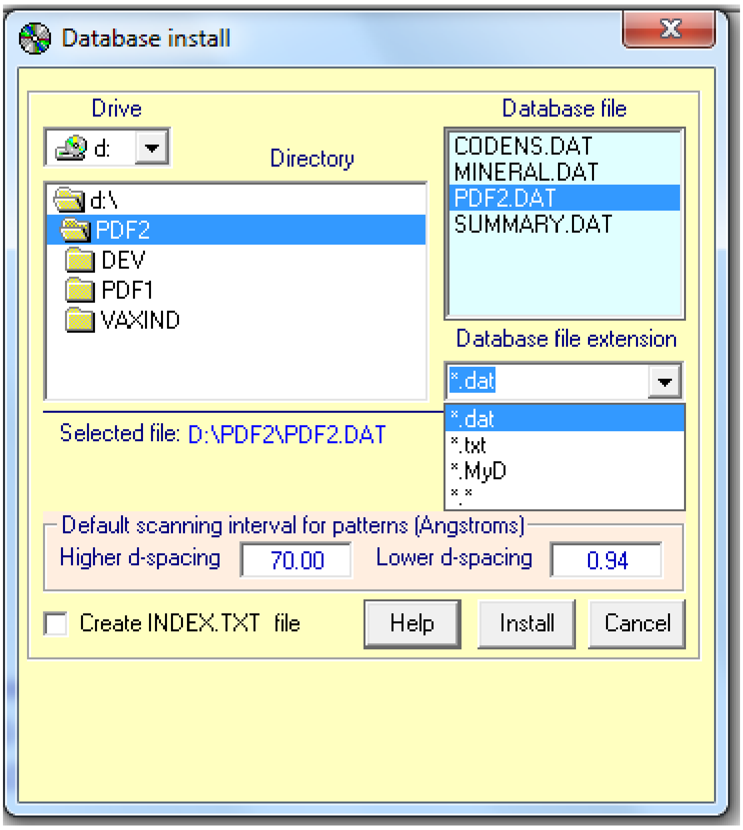


Figure 4

PDF2.DAT. It is the most popular database and is sold by the ICDD. For installation in XPowder only need the file 'PDF2.DAT', because XPowder creates its own index. PDF2 contains several sub-files that include all branches of solid materials used in science and technology:

- Inorganics
- Organics
- Minerals
- Metal and allows
- Common phases
- NBS (National Bureau Standars)
- Forensic
- Educational
- Zeolites
- Explosives
- Super conducting materials
- Cements
- Corrosive materials
- Polymers
- Detergents
- Pigments
- Pharmaceutical
- ICSD
- Ceramics

PDF2 can be purchased at:

ICDD Internet site: www.icdd.com E-mail: info@icdd.com
Postal Address: International Centre for Diffraction Data
12 Campus Boulevard
Newtown Square, PA 19073-3273 U.S.A.
Telephone (610) 325 9814
(610) 325 9814 (General information)
(610) 325 9810 (Sales)

The quality of the PDF2 records is very heterogeneous, since there are diffractograms obtained with different radiation, different geometries or instrumental conditions. There are even not indexed or wrongly indexed phases. They also contain theoretical diagrams calculated from their crystal structures. In general the quality of the records is good and the file is completed and improved year after year.

In order to install the ICDD database, only ‘PDF2.DAT’ file from PDF-CDROM is necessary without any other file index.

DifData.txt. AMSCD database (American Mineralogist Crystal Structure Database) a free database created and managed by Dr Robert T. Downs of University of Arizona. It is limited to minerals. Diffractograms were calculated from the crystal structures published in the scientific literature. In general the quality is high and the database includes many entries of isomorphic series at high temperatures and high and very high pressures.

The records have a homogeneous quality and, although these are calculated, fit well with experimental diffractograms. The biggest errors occur in minerals whose structure and unit-cell were published long ago, as they were based on values of inadequate wavelength or inaccurate tools. This results in systematic errors on calculated d-spacings and hinders the identification. By contrast, diffractograms based structures published in the last few decades are very accurate. The Difdata.txt file does not include chemical formulas in itself (it only indicate the name of a mineral). However, the composition is found in the 'CifData.txt' file provided in parallel and can be loaded prior to difdata.txt installation. Even without this operation, XPowder assigns a chemical formula to correct 96% of the records. Another handicap of this database is the lack of the 'I / Icor' parameter, so XPowder automatically and temporarily assigned a value of 1 to RIR parameter for quantitative analysis.

CifData.txt. is a complementary AMSCD database (American Mineralogist Crystal Structure Database) . It contains the structural and compositional data that have helped generate sheets of diffractograms database 'DifData.txt'. The installation under the program XPowder is not necessary (but desirable). In any case must be installed before the 'DifData.txt'.

P2D2 (Predicted Powder Diffraction Database) is built up by calculating the powder patterns corresponding to the predicted crystal structures from the latest PCOD update. The job is done partly by ZEFSA II (898707 entries) and for the GRINSP data (163520 entries) by the CIF2POW software. The P2D2 database currently includes twelve text files, each with approximately 100000 compounds, which can be automatically indexed by XPowder12, individual or jointly.

MyDatabase.MyD. It is a database that can easily be created and customized by the user, as shown in Chapter 5.

Chapter 1. The main screen

The image of the figure 1.1. appears when you run XPowder.

At the top are provided a drop-down menu (File Edit ...) and tool bar with buttons that perform the main functions of the program.

Under the tool bar is provided the main graph area.

In the middle of the window (blue background) are shown various options and default values (data file, 2θ limits, database options in the main chart, etc.).

At the bottom (orange background) is a second graph area

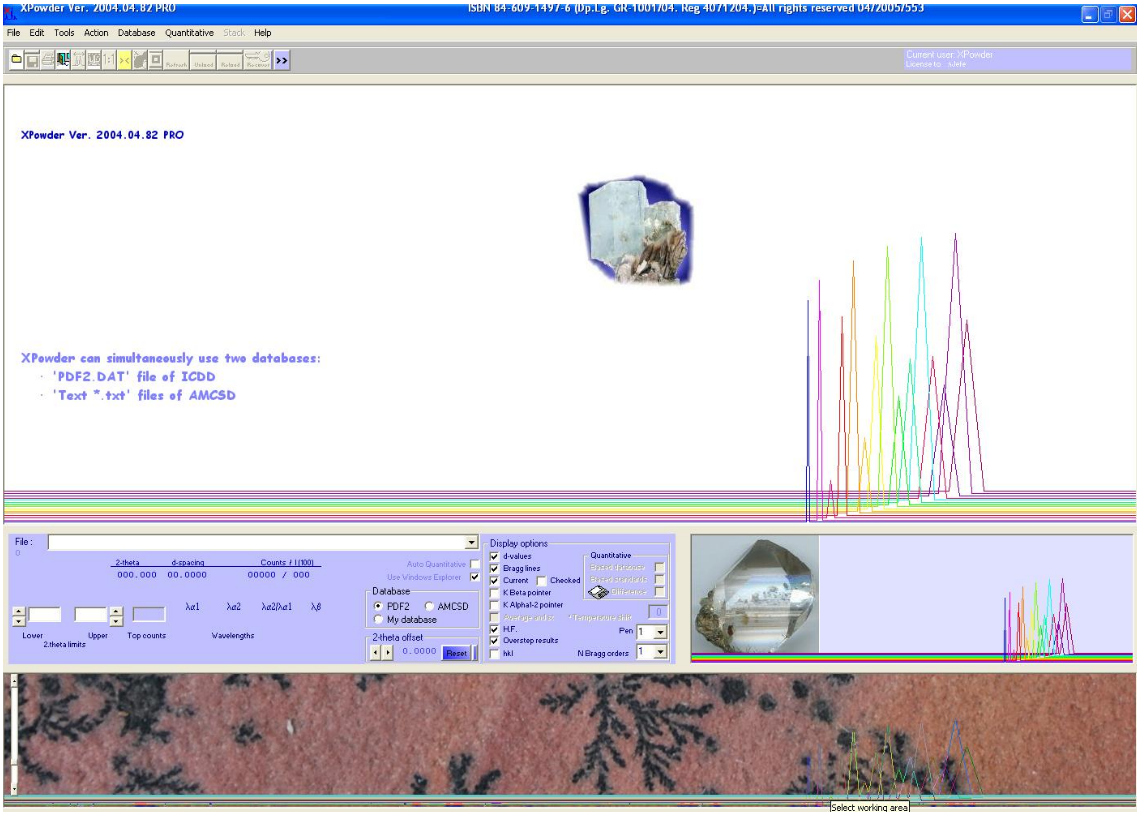


Figure 1.1. XPowder home screen.

How do you open a file?

From the main menu (File -> Open file or pressing the second button (figure 1.2.)

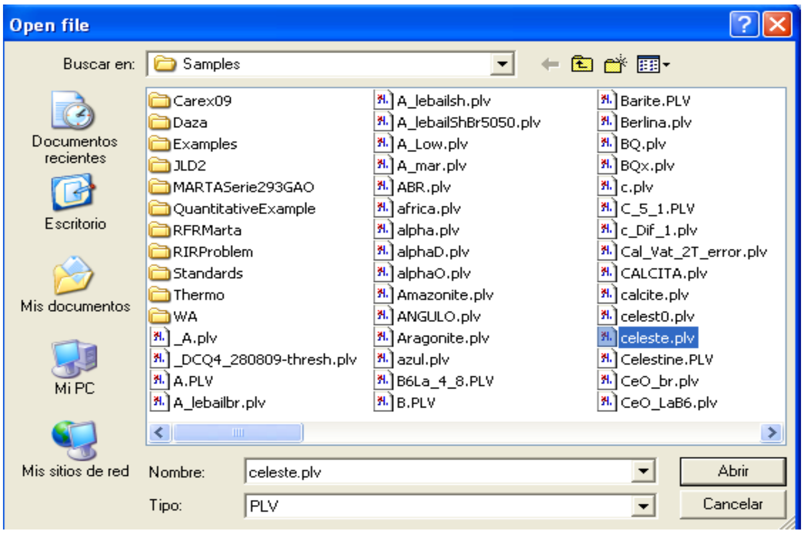


Figure 1. 2.

You can select one or more file samples (A.plv ... D.plv in this example). After clicking OK , you get the figure 1.3.

Figure 1.3. Main screen

Main commands.

Once the files are loaded, a diffractogram is shown in both the upper and lower graphs, while they are activated menu options and some buttons that until now were disabled. On the '*Zoom*' screen is drawn in detail the diffractogram in position near the cursor. The cursor consists of two lines when the box Kalpha 1-2 pointer is marked: The red mark the position $K\alpha_1$ and the green $K\alpha_2$. In the File box have been deployed all four files are loaded. You can select any of them with the left mouse button.

The lower graph shows the entire diffractogram and allows zooming using a 'click&drag' of the mouse. The region of interest is then displayed on the upper graph (for example $49<2\theta^o<56$ in the example of figure 1.4). To zoom directly in the upper graph, the Shift key must be pressed during a left click & drag of the mouse.

On the main graph, a left click of the mouse button adds a peak position that will be taken into account in subsequent calculations (the program can also find peaks automatically).

Figure 1.4.

To restore the full-size diffractogram, click on the button 1:1 or use the contextual menu appears by right-clicking the mouse, as in Figure 1.5.

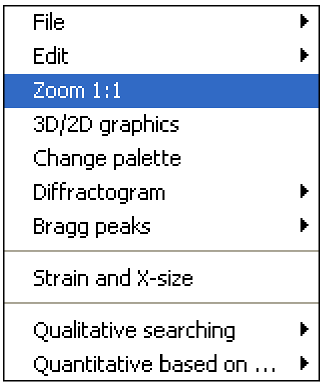


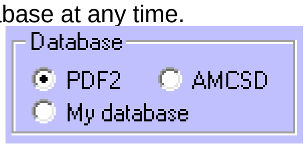
Figure 1.5.

The button can also be used for zooming out.

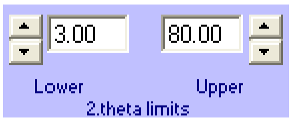
In a similar way many routine tasks can be performed within this graph.
For example:

- Activate the cursor to display the position of Kα_2 K Alpha1-2 pointer, and Kβ K Beta pointer. Also to display simultaneously several Bragg's orders N Bragg orders 1

- Select or change the active database at any time.



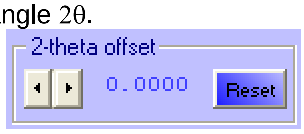
- Enter the lower and upper 2θ limits.



- Show the values of the d-spacing d-values and positions of the peaks Bragg lines in the main graphic, where they have been previously calculated.

- Show HKL indices of the components previously identified hkl in the main graphic.

- Correct the position of zero angle 2θ.



- Calculate the average intensity of a diagram and its standard deviation (useful for estimating the 'crystallinity' overall sample in a simple way) . Average and st

- Identify with one click crystal components in the database with the active restrictions (chemical composition, subfiles, pressure, temperature, etc.).

- Advanced identification of crystalline compounds through restriction of chemical composition, observation window, Euclidean criteria, Boolean criteria, etc. (Chapters 2 and 4).

- Set the chemical and subfiles searching conditions. (Chapter4).

- Display peak positions and intensities of the phase highlighted in the search result window Current

- Display peaks positions and intensities of all mineral selected in the search result window. Checked

- Strip Kα_2 (Chapter 3).

- Subtract the background. (Chapter 3).

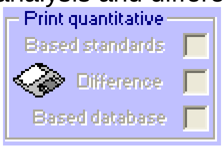
- Smooth the data using Fourier transform smoothing or functional smoothing . (Chapter 3).

- Crop the 2θ interval of the main graph . This action removes the rest of diffractogram from the computer memory.

- Calculate the average intensity and standard deviation of full intensities Average and st.

- Refine the unit cell without operator intervention H.F. .

- Show the results of quantitative analysis and differences on the main screen.



- Save difference diffractogram with text PLV format.
- Acquire data from diffractometer (PLUS version only).
- Calculate or clear the values of d-spacings of full diffractogram. You can also add a peak with a left click or remove a peak by double clicking on it.
- Calculate or clear only the values of d-spacings of main screen selected zone.
- 2θ zero shift correction by standard patterns or harmonic reflections methods (Chapter 3).
- Profile calculations, which include determining the Caglioti function for the sample (or instrument profile), quantitative analysis from the database, depending on the calculation of mixing, Williamson-Hall plot, and so on. (Chapters 10 and 11).
- Estimates of domain size and strain by means of Warren-Averbach methods. Calculating log-normal distribution. It is possible to apply automatically instrumental correcting by using a very crystalline standard or by calculation on the basis of the Caglioti and profile functions. (Chapter 10).
- Select active diffractogram color.
- Palette for diffractogram series.
- Select wavelength values.
- Interpolate experimental data using cubic splines that do not alter the shape of the profiles. It is useful in analyzing profile, unit-cell refinement, etc. (Chapter 3).
- Refine Unit-cell refinement. This option is best done when the samples have been previously identified and also the component $K\alpha_2$ has been eliminated.
- Show pattern series in 2D and 3D (Chapter 8).
- Refresh screen, unload, reload and restore previous search data of actual diffraction pattern, with the 

buttons respectively.
- Reverse or eliminate negative intensities, reverse values, respectively . These are useful for manipulating calculated or differences diffractograms.
- Open files, print graphics and reports, save files, exit program respectively.
- Database install or update.
- Añadir una nueva ficha a ‘Mydatabase.MyD’

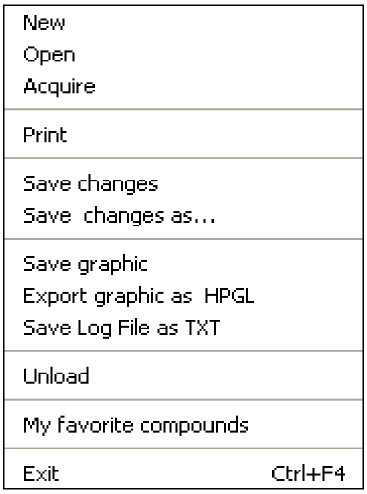
- Occasionally undo the last change 

Small horizontal bars that appear on some command buttons perform the same operations as these, but above all the loaded diffractograms

Menu bar. Is at the top of the screen. It performs many of the button actions described in the preceding paragraph. Most actions can be selected using either method.

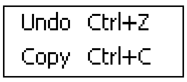
Clicking on any entry in this bar, opens a scroll-down menu:

File



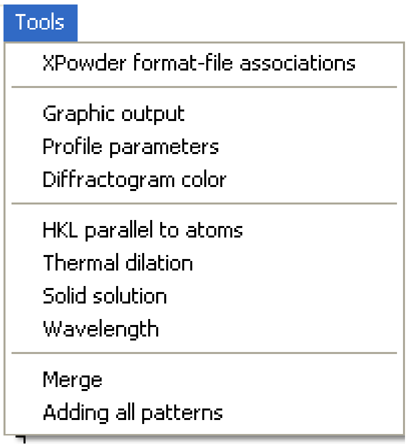
New: Start session.
Open: Load a diffractogram file.
Acquire: Load data from diffractometer (only PLUS version).
Print: Print graphics and scripts..
Save changes: Save changes of diffractogram data.
Save changes as...: Save changes a diffractogram data with a different file name.
Save graphic: Save BMP image of active graphic with the computer screen resolution.
Export graphic as HPGL. Create and save a HPGL (plo*tter file) that can be exported from some graphics programs like Corel Draw*.
Save Log File as TXT. Create a text file that contains an echo of the calculations made and the results,
Unload. Download the actual diffractogram of the computer's memory.
My favorite compounds: To retrieve results of prior qualitative analysis (. RES for the PDF2 database and .RUF for the AMSCD database)
Exit: closes the application

Edit



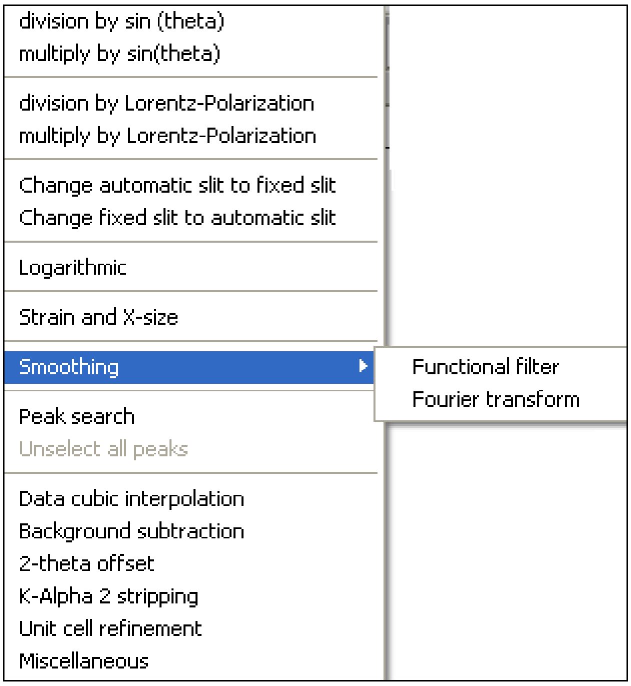
Undo Ctrl.+Z: Undo last change
Copy Ctrl.+C: Copy the diffractogram graphic on the clipboard.

Tools



XPowder format-file associations: Allows associate files with extensions of the program XPowder so they can be opened automatically when you double-click on them in Windows Explorer or the desktop.
Graphic output: It sets up the options and features to be included in graphics printouts.
Profile parameters: Shows the parameters of the profiles of the reflections, both the active as the profile of the instrumental diffractometer. The values can be changed, but are not calculated from this option (for this we must use the button  (Chapters 10 and 11).
Diffractogram color: Set de active diffractogram color.
HKL parallel to atoms: Calculates the indices HKL of a face parallel to two structural or morphological addresses.
Thermal dilation: Calculates the thermal expansion coefficients if diffractograms are obtained at different temperatures. This tool operates automatically on the screen 2D, when used thermodiffraction.
Wavelength: Set wavelength values
Merge: Graphically sum or subtraction of diffraction patterns.
Adding all patterns: Calculate the average diffractogram of all loaded pattterns.

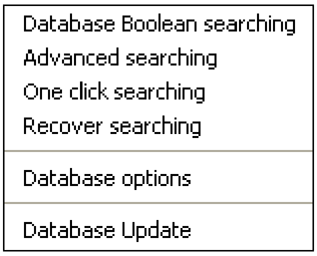
Action



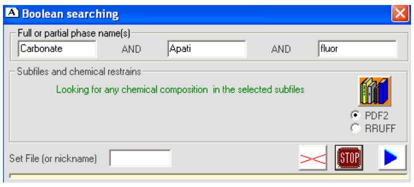
division by sin(theta): Can simulate a change from fixed to automatic slit.
multiply by sin(theta): Can simulate a change from automatic to fixed slit.
División by Lorentz-Polarization: Performs Lorentz-polarization factor correction of powder diffractograms. It is useful in profile analysis.
Multiply by Lorentz-Polarization: Reverse of the previous operation.
Change automatic slit to fixed slit. Simulates the change from automatic to fixed slit in Bragg-Brentano geometry. The used function is : $\mathbf{I}_f = \Delta^o \cdot 0.20268 \cdot \mathbf{I}_a / \sin(11.16+\theta^o \cdot 0.88-0.19)$
($\mathbf{I}_f$ = Intensity measured with fixed slit, $\mathbf{I}_a$ = Idem automatic slit, Δ^o = divergence fixed slit).
Change fixed slit to automatic slit: Reverse of the previous operation.

Logarthmic/Aritmetic: Puts the intensities axe in logarithmic/arithmetic scale. Its use is highly recommended to localize reflections of low intensity, on very low crystallinity materials or having a great orientation. Use the arithmetic scale for qualitative and quantitative analyses. Do not carry out operations such as' Ka2 stripping, subtraction of database profile cards, etc,. when using the logarithmic scale.
Strain and Size: Profile analysis general tools.
Smoothing: Removes noise through functional and Fourier transform filters.
Peak search: Search maxima of Bragg reflections
Unselect all peaks: Unselect Bragg reflections.
Data cubic interpolation: Make a spline cubic not distorting, which allows interpolate experimental data without changing the shape of the profiles. It is a very useful filter.
Background subtraction: Perform background subtraction automatically.
2-theta offset: Tool for the correction of zero on the scale of 2θ, using internal standards or harmonics.
K-Alpha 2 stripping: The component $K\alpha_2$ of diffractograms obtained with X-ray tube is removed. It is necessary for many calculations profile based on widths of reflections and highly advisable before unit-cell refinement.
Unit cell refinement: Automatic unit-cell refinement.
Miscellaneous: Profile calculations, which include the Caglioti function fitting for the sample (or instrument profile), quantitative analysis from the database, depending on the calculation of mixing, Williamson-Hall plot, and so on. (Chapters 10 and 11).

Database



Database Boolean searchig: Allows a manual search of records from the database by 'Set-File', key words, names, chemical composition, and so on. This example shows how to search apatite containing fluorine and carbonate anions



in the base PDF2 with the options active ( ) which are explained in Chapter 4. If the PDF2 set and file '5 586 ' are introduced in the box Set File (or nickname) , the program will return the record of the mineral calcite. If this box is introduced any nickname, described in the file 'Favorites.txt', or part of it, the program will return the record with the same nickname (Chapter 12).

Advanced searching: Advanced identification of crystalline compounds through restriction of chemical composition, observation window, Euclidean criteria, Boolean criteria, etc. (Chapters 2 and 4).
One click searching: Identify with one click crystal components in the database with the active restrictions (chemical composition, subfiles, pressure, temperature, etc.).
Database options: Set the chemical and subfiles searching conditions. (Chapter 4).
Database install (or Database Update): Allows you to install (or reinstall) a database (PDF2.DAT or DifData.txt).

Home

Chapter 2. Searching advanced options

This section (Figure 2.1.) is accessed from the main screen(Figure 1.3.) by clicking on the button .

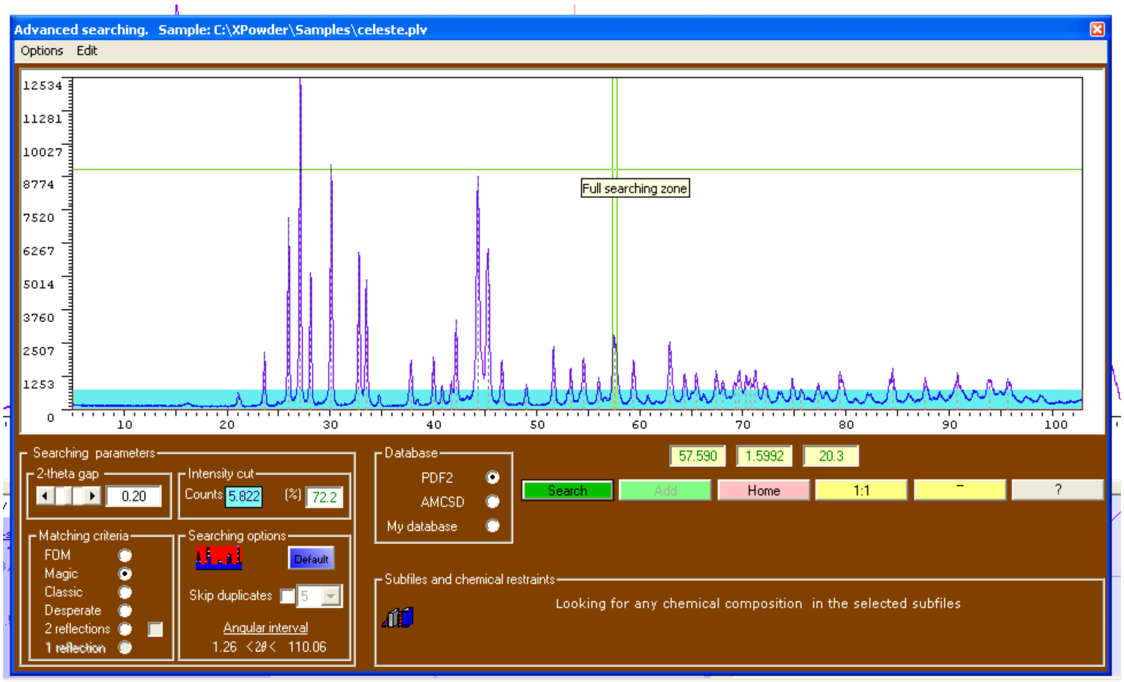


Figure 2.1.

The graph of this screen shows the diffractogram with the zoom level used in the main screen. You can get a greater detail by pressing the Shift key and dragging with the left mouse button on the chosen area. The button 1:1 rescale the diffractogram to full size, while the button - diminish the scale gradually.

When you move the cursor on the graphic the values 2θ, spacing and intensity show respectively in the three boxes (back yellow , green numbers) are located above the key Main.

The sky blue area of the bottom of diffractogram 'hidden' reflections of lesser intensity. The optimum height is calculated by the program itself. The peaks hidden will be taken into account during the search but as an incidental, so that components minority might go unnoticed in these conditions. The height of the blue zone can be changed by clicking on the desired height with the left mouse button. The value of cut is reflected in the box Intensity cut. The sky blue area can be overridden by pressing the button , or restored to its original value with Default. It is convenient to use the blue zone during the early stages of identification in samples with many components. In later stages, and without it you can establish the components minority.

When you check the box Skip duplicates 5, you can select the first N letters of the name of a crystalline phase, so that the program will choose the best card in the database for that chain letters. In the example, assume that the sample contains the mineral 'Celestine', which is ten or more records in the PDF database, and five in the AMSCD database, will show only the best suited and whose name begins with the string 'Celes' (5 characters). The program distinguishes between phases removed from the database (Deleted in PDF2) of the active. Thus, identifying where the criterion be applied Skip duplicates show results as possible 'Celestine' and 'D Celestine' in the example above. The first letter D is used to mark the card as deleted. If during the search you want to discard the deleted records see Chapter 4.

Within the framework of search parameters Searching parameters you can select the interval 2-theta gap that the program used to consider as a reflection observed.

This value corresponds to the width (2q th) of the distance between the two vertical green lines in Figure 2.1. It is appropriate that this value is given to excess. Very small values may prevent some compounds are not 'observed,' what happens when diffractometers are poorly aligned or records from the database are of low quality. The default value (0.20) is usually valid for the majority of cases.

On this screen you can select the active database (PDF2 o AMSCD).

The order  allows you to select specific subfiless within each database (minerals, organic compounds, and so on, inside PDF2, or PT conditions within AMSCD) and chemical restraints (for example, you can search for Fe, Mg or Ca carbonates). The use of this tool is shown in Chapter 3. The restrictions were activated show next to this icon (looking for... en la Figure 4.1.).

Matching criteria box lets you select between four criteria for identifying phases. All of them are based on numerical taxonomy methods in a multidimensional space where, the minimum Euclid hyperdistances (**H**) between the data of problem diffractogram (**M_o**) and of the database (**M_c**) are calculated. The differences between the methods lies in the different ways in which defines the axis of multidimensional space:

$$\mathbf{H^2 = \sum (M_o - M_c)^2}$$

To find **H**, you must use only reflections inside the 2θ selected interval. Therefore, the zoom should not be used to analyze the complete diffractogram in searching procedures. The zoom should be used only when you want to identify reflections and isolated minority phases.

- FOM . The axes contain 'figures-of-merit' dependents of 2θ-zero error of diffractogram. Should not be used when the diffractomet is badly aligned or the database records are poor quality.

- Magic . The axes contain 'figures-of-merit' independents of error of zero difractometer, the database and the coincidence of reflections from various crystalline phases. Often the most effective approach for identification.

- Classic .The axes contains d-spacing values, although XPowder automatically corrects the corresponding values of the databases, agree to normalized experimental conditions, before proceeding to the calculation of hyperdistances. This criterion should not be used this approach when there are many similarities between 2θ angles of different components, the difractometer is poorly aligned or database records are of poor quality.

- Desperate. The program uses only two reflections of experimental diagram and optimizes its agreement with the database. Should be used only in diffractograms of very low quality or for minor phases. The second option approach 'Desperate' is not affordable by the user, but is selected exclusively by the program itself in cases that do not appear obvious solutions or when you have selected a single reflection of the experimental diagram.

- 2 reflections. Since version 2004.04.54 has been including a new approach that uses only two of the diffractogram reflections to maching with the high intensity reflections of database records. When this option is used, the number of possible solutions is high in general, due to the lack of information used in the calculations. It is therefore appropriate to provide supplementary information to the program (about chemical composition, for example). This approach should be used in diffractograms having small scaning intervals (eg 2 <2θ <50 °), or for identication of minority phases. Also, from version 2004.04.54, the second searching options of 'Desperate' has been

renamed to '1 reflection' , because it uses in searching one selected reflection only. (See updates).

The hyperdistance value (H) is considered by the program as a key criterion for the identification and its value appears in the output table ('Matching' tool, Chapter 5).

The search begins when you press the button Search. Alternatively you can complete the list of subsequent phases identified with the button Add. The button Main does the program go back to the initial screen without performing any search.

The ability of this program to search for and identify compounds is high because of their special characteristics:

- The algorithm that uses the approach *Magic* improves, more than any other, both the quality of experimental data as those from the databases.
- During the search process (searching), XPowder standardizes the value of the wavelength. To do so reads the value of radiation used in each database record and correcting the position of maximum for the radiation used in the diffractogram problem, regardless of d-spacings write in the database. The process takes place even if the discrepancies in values of wavelengths are minimal. For example, some records have been obtained with wavelength $K\alpha_{average}$, while others have been developed with $K\alpha_1$ or even with other radiation differently. This does not affect the algorithm for calculating used by XPowder, but the criteria used by other searching programs.
- After obtaining the best match by calculating hyperdistances, a second approach is performed. Then, each database records is adjusted to the experimental by nonlinear least-square methods. The their possible misalignments of 2θ are refined again. The standard deviation obtained during the procedure allows to specify the phase, within the list of substances identified by the calculation of **H**. Furthermore, adjusting the fractions (**f**) of the mixing function (**F**) of each component (**c**) for each angle θ, so that:

$$\mathbf{F_\theta = \left(\sum I_{c\theta} \cdot f_c\right) / \sum f_c}$$

  $\mathbf{I_{c\theta}}$ are the intensities of each component in the angle θ**.** Therefore, allow $\mathbf{f_c}$ values estimated preliminary weighting of each component between 0 and 1 (see Figure 5.2: $\mathbf{f_c}$= Weight=0.75 corresponds to the weight of celestine in the global mix function).

These operations, unlike those used in the calculation of **H**, are made on the whole diffractogram, whatever the used zoom.

- The results are displayed in a single list (Chapter 4) that can interact graphically (matching) with the experimental diffractogram. Optionally, you can subtract gradually phases identified in the original diffractogram (see Chapter 5. Card profile , Figure 5.7). This, which is not normally required, can occasionally facilitate the identification of minority components. On the other hand, can be superimposed graphically diagram experimental records from this list, one at a time, or all considered correctly identified.

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Chapter 3. Pattern filtering

In general there is no need to make any special treatment from the diffraction data, but when the experimental conditions are not ideal, some tools can be used to improve quality.

1. Zero 2θ offset angle correction.

(See also update 2010.01.10: Planar CCD geometry, Polynomial 2θ fit)

XPowder has two methods to to correct the error of 2θ zero:

- Correction with internal standard.

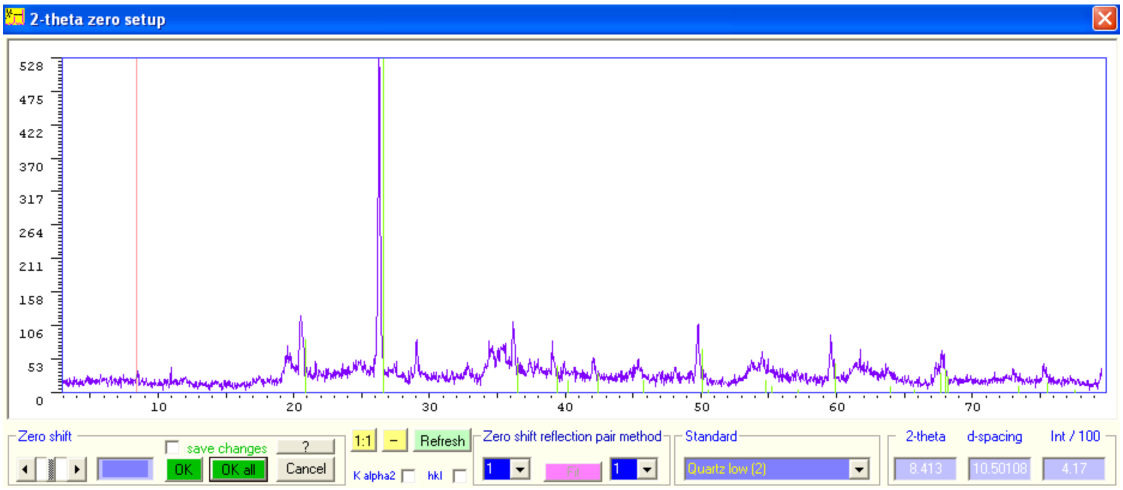


Figure 3.1

In Figure 3.1. an internal standard, which can be selected from the list of the frame Standard (*Quartz low (2)* in the example), is used to verify experimentally the displacement of 2θ. The internal standards can be included in the file manually 'std.txt' as described in chapter 12.

You can 'zoom' on the area 20<2θ<30 for more precisisón (Figure 3.2).

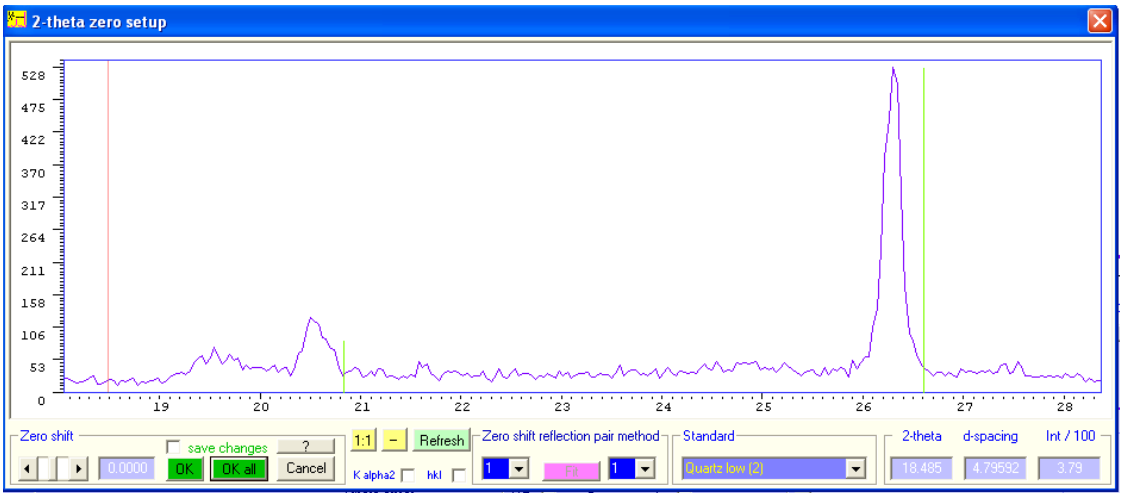


Figure 3.2.

With the tool  can move the diffractogram its true position (Figure 3.3) and shows the movement made (-0.0480) in the framework Zero shift .

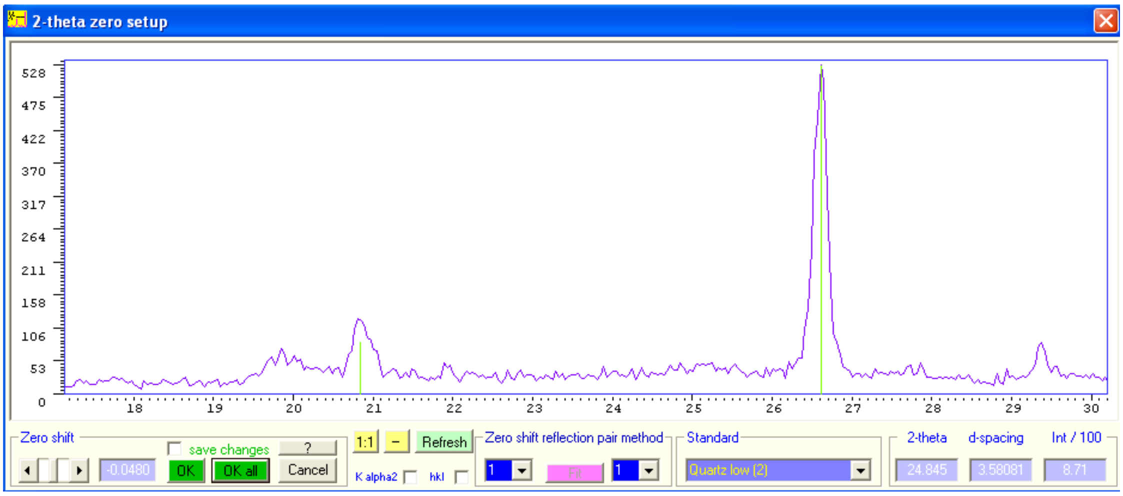


Figure 3.3

- <u>Correction $\Delta 2\theta$ through harmonics</u>.

To apply this method will require two different orders of a reflection, that appear on the angles θ_1 and θ_2 respectively.

When there is a shift of the origin Δ_θ of the scale of the angle θ, the equation of Bragg requires:

$n_1 \cdot \lambda = 2\, d\, \mathbf{sin}(\theta_1 - \Delta_\theta)$

$n_2 \cdot \lambda = 2\, d\, \mathbf{sin}(\theta_2 - \Delta_\theta)$

$N = n_1/n_2 = \mathbf{sin}(\theta_1 - \Delta_\theta) / \mathbf{sin}(\theta_2 - \Delta_\theta)$

$N = (\mathbf{sin}\theta_1\, .\mathbf{cos}\Delta_\theta - \mathbf{cos}\theta_1\, .\mathbf{sin}\Delta_\theta) / (\mathbf{sin}\theta_2\, .\mathbf{cos}\Delta_\theta - \mathbf{cos}\theta_2\, .\mathbf{sin}\Delta_\theta)$

If numerator and denominator are divided by $\mathbf{cos}(\Delta_\theta)$

$N = (\mathbf{sin}\theta_1 - \mathbf{cos}\theta_1 \cdot \mathbf{tan}\Delta_\theta) / (\mathbf{sin}\theta_2 - \mathbf{cos}\theta_2 \cdot \mathbf{tan}\Delta_\theta)$

$\mathbf{tan}\Delta_\theta = (\mathbf{sin}\theta_1 - N\, \mathbf{sin}\theta_2) / (\mathbf{cos}\theta_1 - N\, \mathbf{cos}\theta_2)$

it appears the error of angle 2θ.

$\Delta_{2\theta} = 2 \bullet \Delta_\theta$

To carry out the correction, you should select two orders of a reflection of Bragg (could be any, even non-consecutive reflections) within the frame Zero shift reflection pair method. In Figure 3.4, have been selected respectively orders 1 and 2 (you'll see the cursor corresponding graphs from n = 1 to 2). By placing the cursor n = 1 on the first reflection (approximately 18.6 degrees) shows that the position of second order is not correct (the second cursor, approximately 17.7 degrees). Pressing Alt + left mouse button is a utomatically carries out the correction, as shown in Figure 3.5.

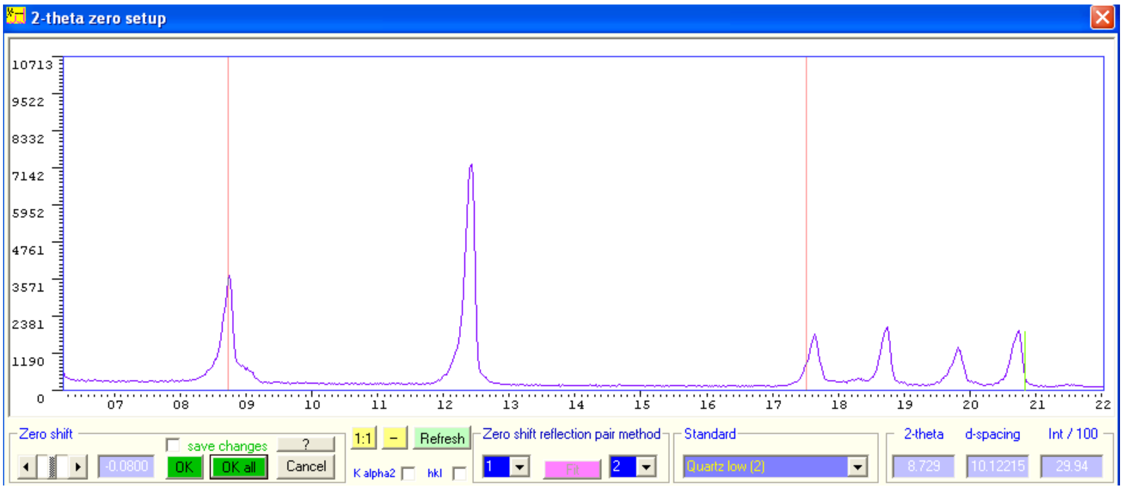


Figure 3.4. Before correction of zero 2θ.

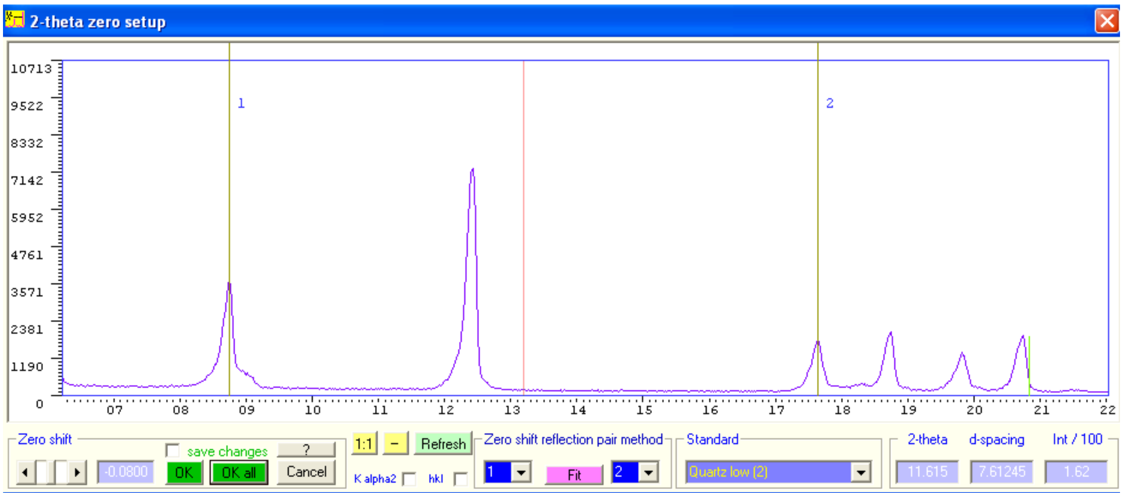
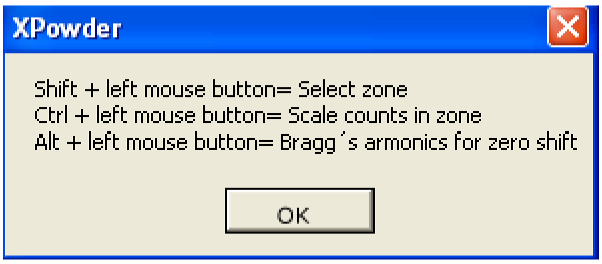


Figure 3. 5. Has been detected and corrected a displacement of -0.0800 º. The correct positions of the two reflection orders are marked with their respective values of n.

In either of the two methods described, when pressed OK , the program returns to the main screen. OK all states the same correction for all samples are loaded into memory (up 50). If the box save changes is selected, in addition to the above, the data files are saved on your hard drive. Cancel rejet the changes. ? shows a help on using this screen).



2. Elimination of noise.

Lets remove small and frequent fluctuations of the diffractogram registration. Any action of this type should retain the geometry of the profiles, which otherwise would leave inoperative diffratograms ir order to study of profile analysis. XPowder uses two methods:

- Functional filter. There is an average weighted by a continuous distribution function characteristic of the diffractogram. Every calculation is done automatically by pressing the button  or menu '*Action -> Smoothing -> Functional filter'*

- Fourier transform. Removes higher frequencies in the Fourier transform using a cutoff value and then calculates the inverse transform, which gives us the filtered diffractogram. Is accomplished by pressing the button  or menu '*Action -> Smoothing -> Functional filter'*. The Figure 3.7 shows how to handle tool for the Fourier filter.

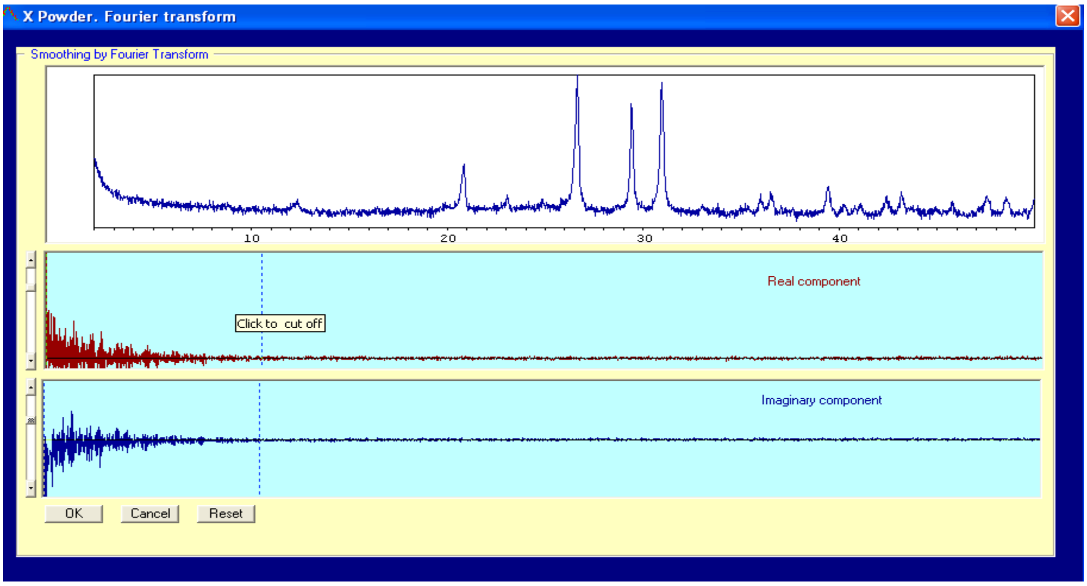


Figure 3.6. Clicking on the position of the cursor eliminates the frequencies located on your right and you get the filtered image of Figure 3.8.

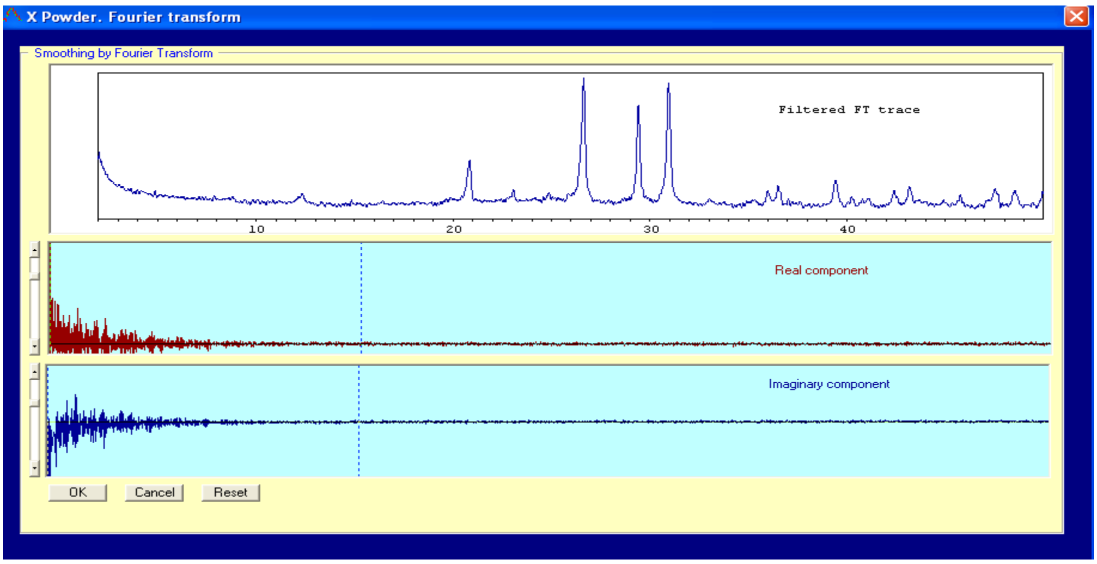


Figure 3.7. The smoothed diffractogram can be seen at the top.

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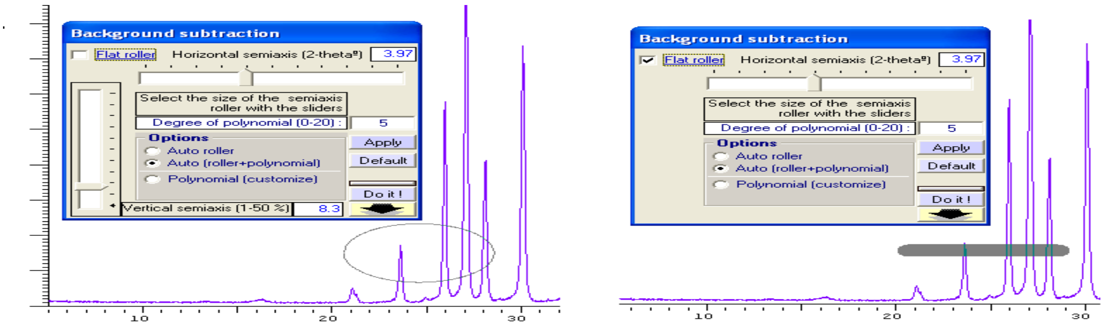
3. **Background subtraction.** .



A **Figure 3.8.** **B**

An **ellipse** (Figure 3.8A, Flat roller box unchecked) or a **segment** (Fig 3.8B, Flat roller box checked) can be used interchangeably, to automatically search for points where the background polynomial will be calculated by LS methods. The horizontal cursor (*and/or vertical*) provide the magnitudes of the semiaxes of the ellipse (*or segment*) that will cross the lower diffractogram and whose contact points will be used to calculate the background function by *splin* (Auto roller*), splin + polynomials* up to grade 20 (autoroller+polynomial) or tracing the background of manually selected points (Polynomial customize). The buttons  perform background subtraction on the active diffratogram (*large button*) or on all diffractograms loaded (*top bar*) with the selected options. Figure 3.9. and 3.10. Large ellipses yield a soft elimination of the background while small ones suppress the background completely. Different ellipse sizes should be tried.

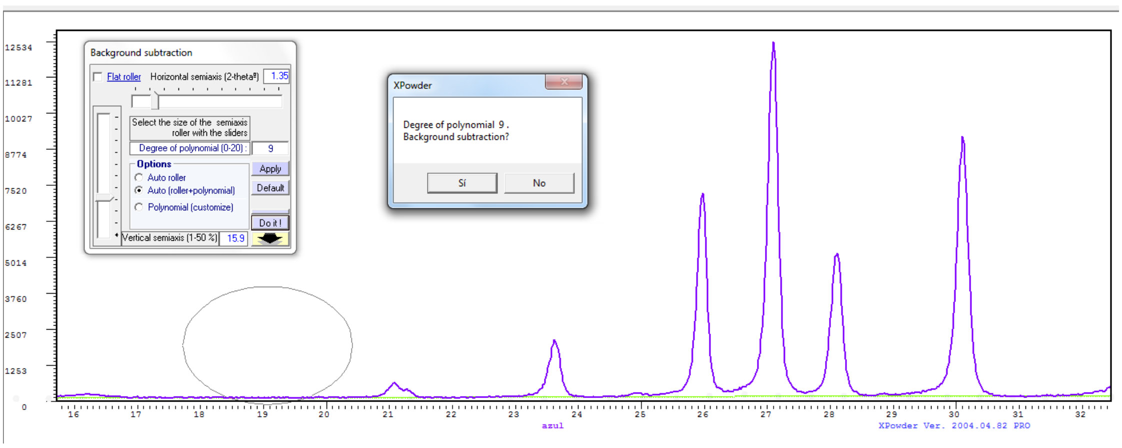


Figure 3.10.

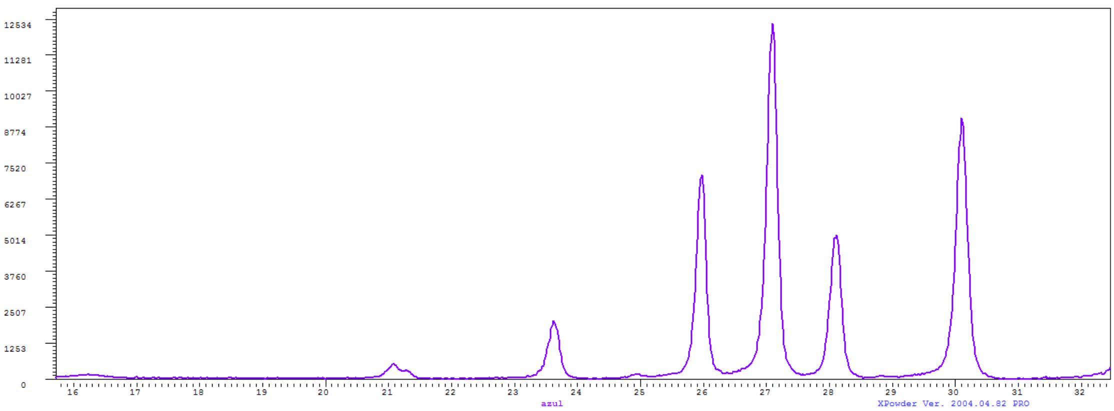
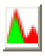


Figure 3.11.

4. <u>Kα_2 stripping</u>. 

It uses the Rachinger method in its classic form, or in a dynamic modification that optimizes the adjustment of the distribution functions of the profiles that are *Kα_2-stripped* in succession during the 2θ scanning. The method 'Advanced', which uses methods of Fourier on reciprocal histogram, is temporarily out of order in the current version.

For proper Kα_2 stripping, use very accurate values of λ_1 , λ_2 and [$I\lambda_2$ / $I\lambda_1$] (use  when necessary).

The process is applied to a diffractogram (XPowder_program_dir\Examples\Quartz60_70.plv) that shows the quartz reflections 113, 300, 212, 203 and 301 (figures 3.12 to 3.14).

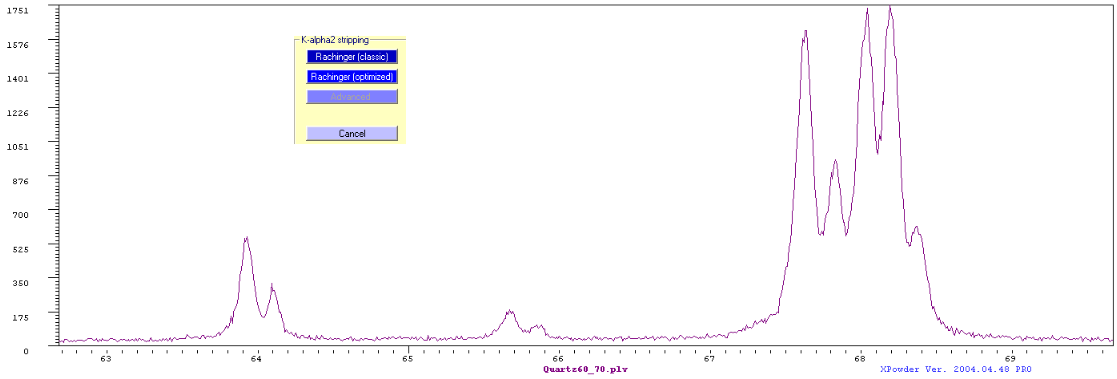


Figure 3.12.

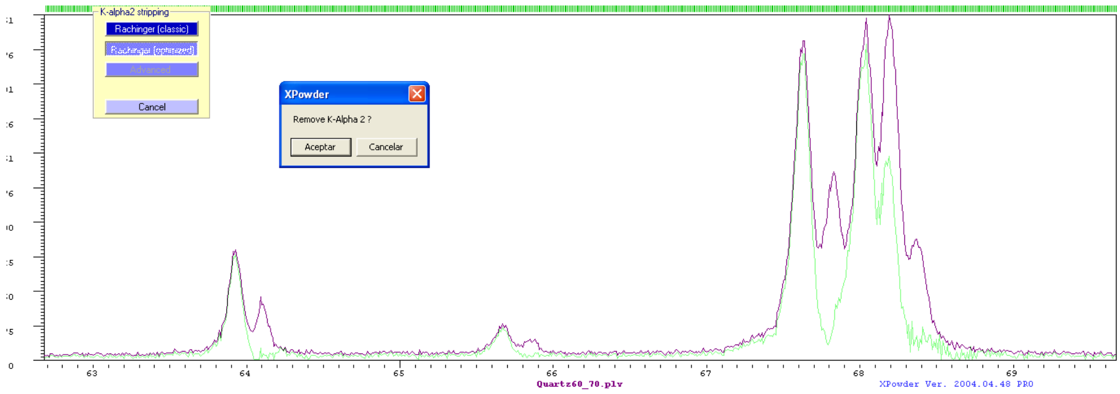


Figure 3.13.

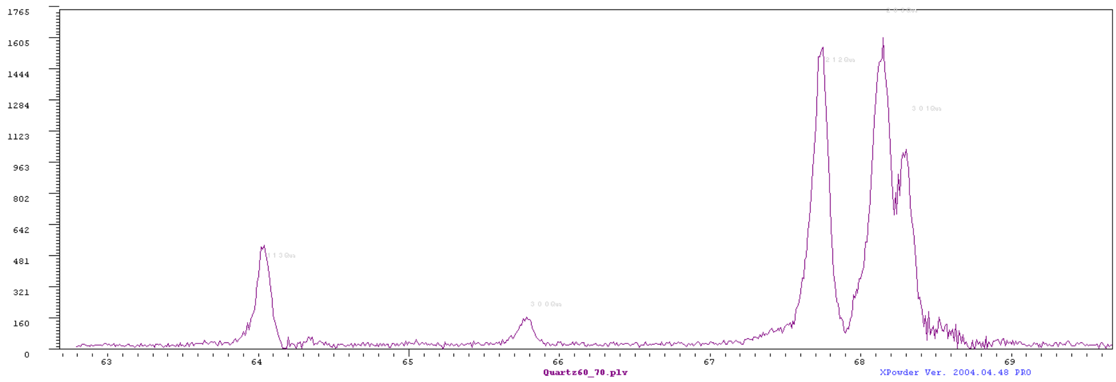
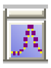


Figure 3.14.

5. Changing 2θ step. 

This procedure significantly improves, without the slightest deformation of the profiles, the quality of measured with an excessive step diffractograms. This operation is very useful, as it happens prior, to improve the quality of $K\alpha_2$ *stripping*, profile analysis or unit-cell refinement Figures 3.15 and 3.16).

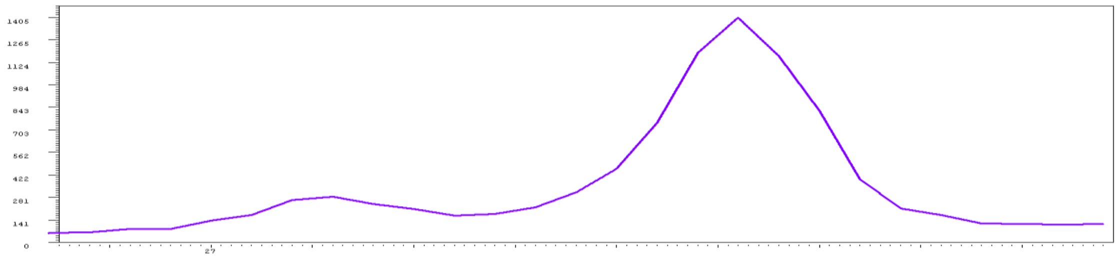


Figure 3.15.

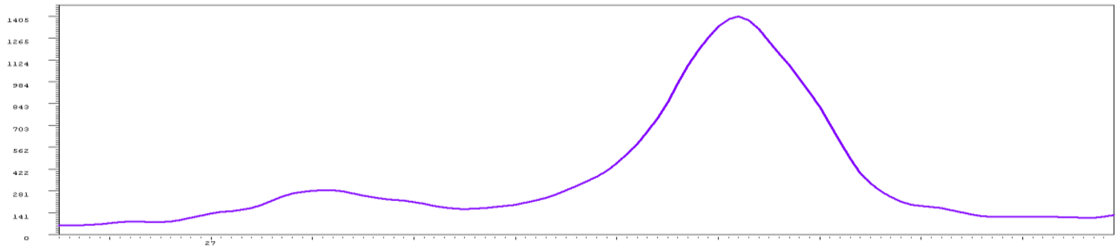


Figure 3.46.

6. Merging diffractograms (Main menu –> Tools -> Merge)

This routine makes weighted additions and subtractions of diffractograms.

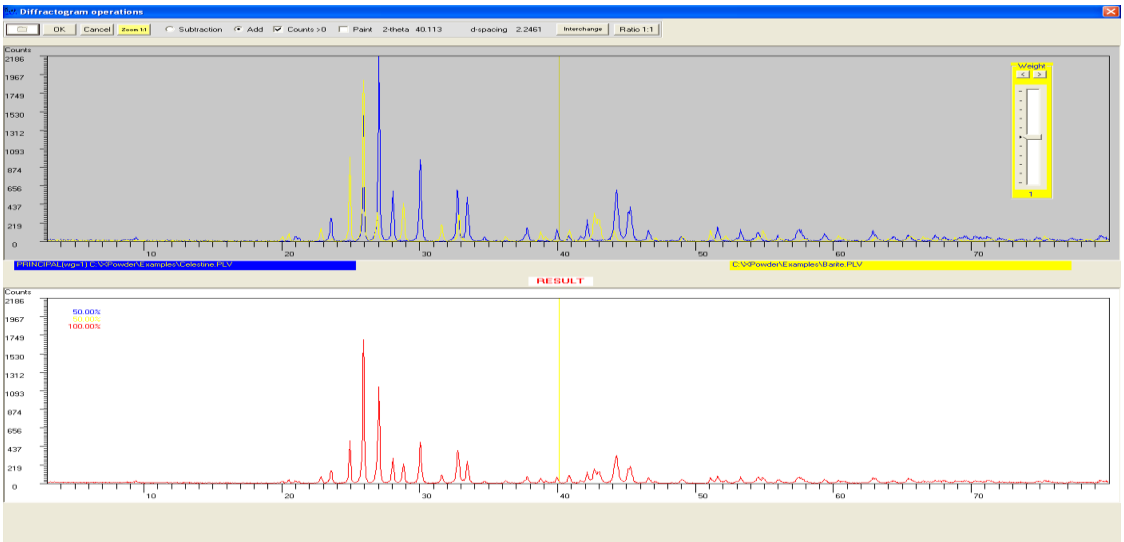


Figure 3.17.

You can add ADD or subtract Subtraction diffratograms. The top of the Figure 3.17 shows the main diagram in blue and the secondary in yellow. The bottom image shows the sum of 50%.

OK Moves diffractogram calculated to the main screen. Caution: The program maintains the same file name that was the main diagram.

Cancel Discard all operations and returns to the main screen.

Zoom 1:1 Lets scale the charts to the original size. It is used when it has made 'zoom' up on this screen.

Paint Fill color the main diffratogram.

Interchange Swap the main and secondary diffractograms.

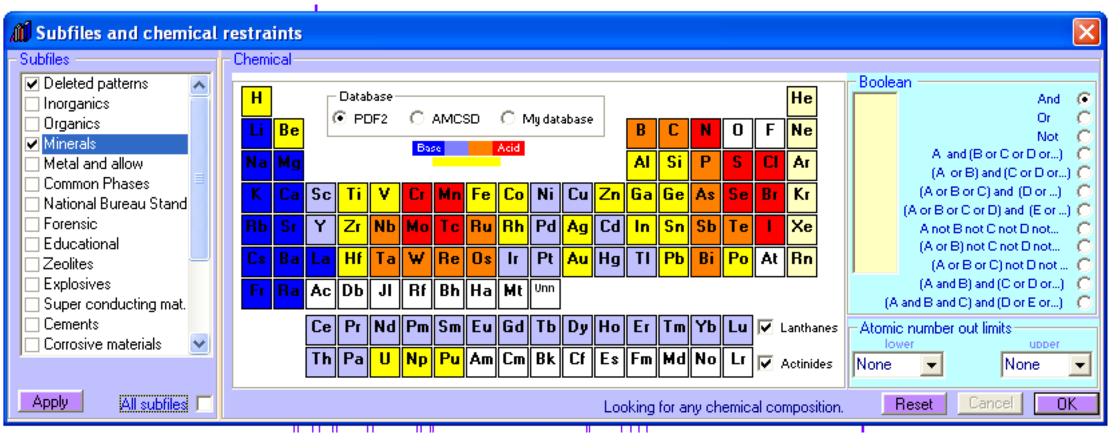
Ratio 1:1 The two original diffractograms have the same weight.

Weight Slider cursor that lets ponder the diagram secondary.

Home

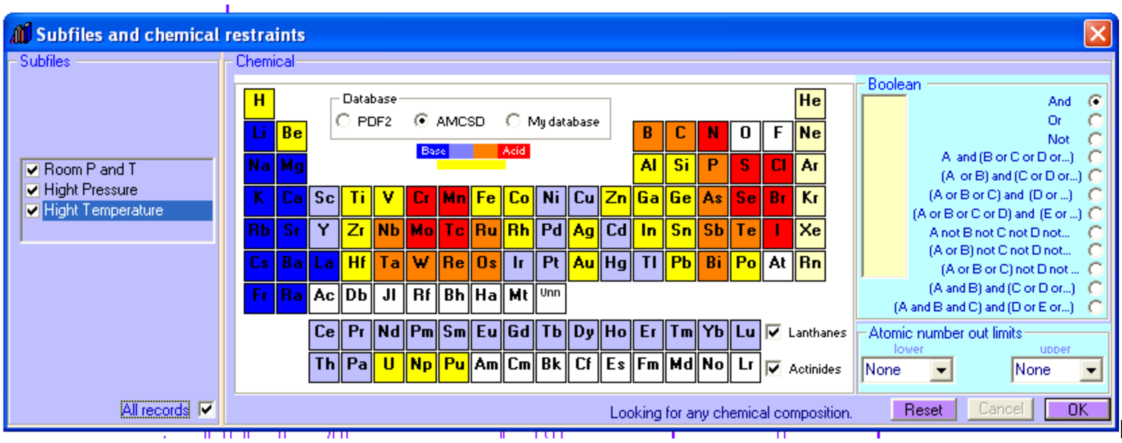
Chapter 4. Searching subfiles and chemical restrictions.

The entrance to this screen (Figures 4.1. y 4.2.) from the 'main screen' or from other parts of the program by clicking the button (Advanced Options on qualitative analysis).



F

Figure 4.1. PDF2 advanced seaching options



F

Figure 4.2. AMSCD advanced seaching options

On both screens, the database can be exchanged, select subfiles or put restrictions on chemical composition using Boolean logic (And, Or, Not and combinations).

The subfiles of each database are selected in the box Subfiles. The **Apply** button in Figure 4.1. establishes what the selected subfiles will be loaded the next time you start XPowder (default setting when using PDF2).

Chemical restrictions:

In a general way you can discard previously in searching phases containing elements lanthanides or actinide (leaving unmarked respective boxes), elements with atomic number Lower than stated, or higher than those given in Upper box. The hydrogen is excluded from these restrictions.

Boolean conditions:

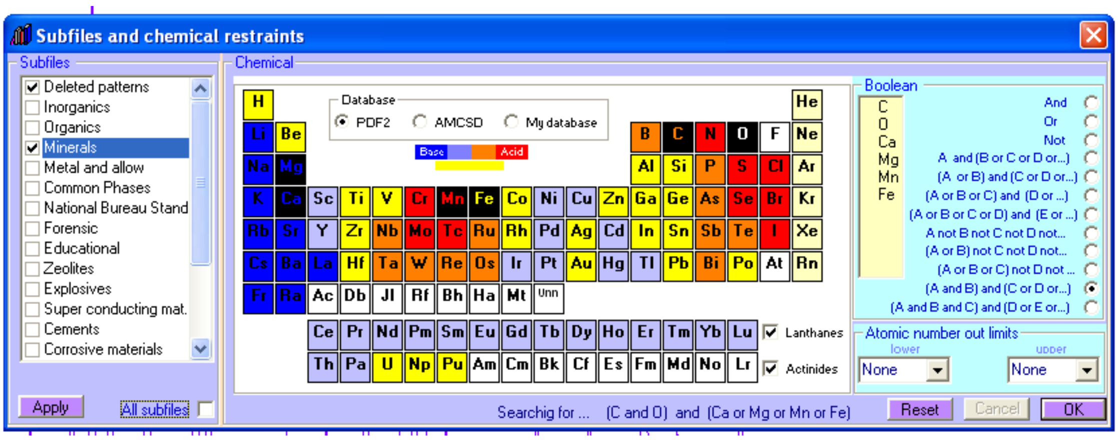
You can choose up to 11 different chemical elements that are involved in the search for components of the sample. To select just click on the symbol in the periodic table of Figures 4.1. or 4.2. A new push on the box, delete the item from the list. **Reset** button removes the list. All items selected must into the chemical composition of the crystalline phase.

- And: All selected elements must into the chemical composition of the crystalline phase.
- Or: At least some selected element should belong to the chemical composition of the crystalline phase.
- Not: None of the selected elements must belong to the chemical composition of the crystalline phase.
- Logical combinations: The three previous operators can be combined by selecting one of the options under Boolean framework. It should be noted that the brackets have priority over the logical operators and therefore, any operation between parentheses will be carried out before the rest. The order in which chemical elements are selected is the same generic sequences of A, B, C, etc. displayed within each of the options under Boolean .

Example

Figure 4.3 shows, for example, how to find carbonates Mg, Ca, Fe or Mn in the subfile 'Minerals' of the database PDF2. The deleted patterns will be taken into account during the search, as indicated in the subfile framework. The selected items are drawn with black background in the periodic table and the sequence is on the list of yellow background, under the title of Boolean framework. The complete logic condition appears developed in the bottom of the screen:

Searchig for … (C and O) and (Ca or Mg or Mn or Fe)



F

Figure 4.3. Chemical searching restriction with PDF2.

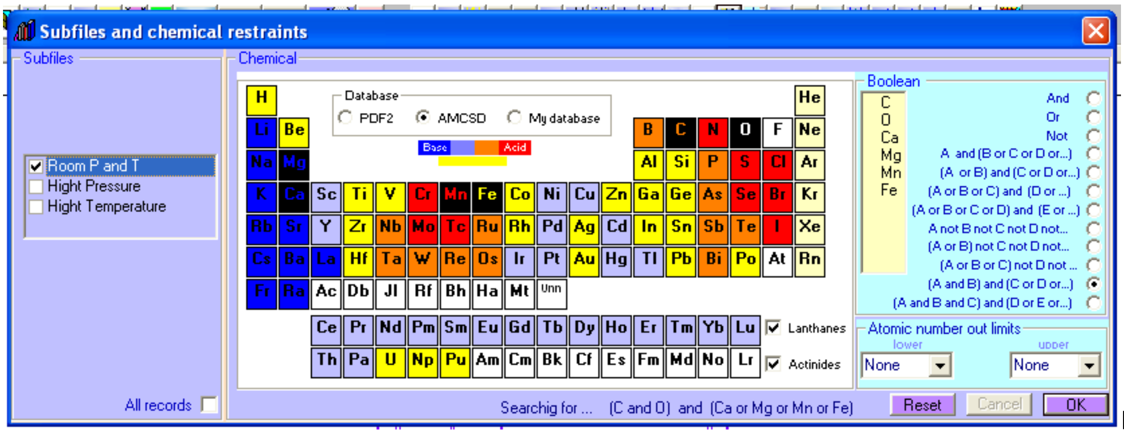


Figure 4.4. Chemical searching restriction with AMSCD.

Figure 4.4 shows the same as in Figure 4.3, but with AMSCD database. In this case, the searching will be made on minerals formed at room temperature and pressure.

The **OK** key confirms the search conditions selected, while **Cancel** ('disabled' in the examples) ruled out any changes made, but does not affect the selection of subfiles.

Home

Chapter 5. *Searching and matching*.

The identification (searching) of substancescan be obtained from the home page (Figure 1.2) manually by using the 'Database-> Databse Boolean Searching "and automatically with the keys (One click searching) or (Advanced searching):

This button performs the search completely automatically, using the search options active at that time (see Chapter 4).

This button will display 'Advanced Options' described in Chapter 4, before performing the search.

In all cases, the results appear on a 'floating' list into the tool Matching, critical to correctly identify and confirm the crystalline components (Fig. 5.1).

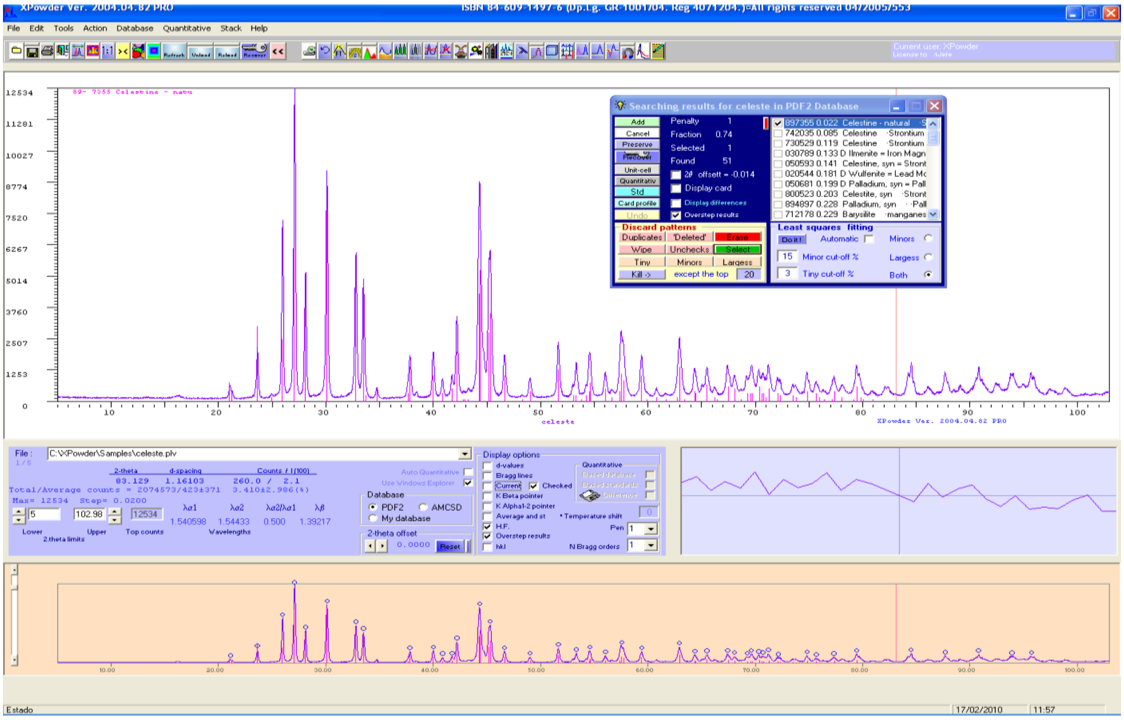


Figure 5.1.

Figure 5.2 shows the tool Matching (ver 2004.04.57) in detail. The example was created from a sample of monomineric Celestine - Sr (SO4) after using the key (*One click searching*) on the mineral PDF2 subfile, including the *deleted phases*. Each file contains from left to right, a check box where it should be confirmed (☑**)** the presence of the mineral. Then there are a six number string that correspond to the 'Set' (first two digits) and 'File' (the other four) of the database. The following is the *Euclidean hyperdiste* that has allowed the identification (smaller is better in terms of the adjustment). Following is the name of the previous stage, or not, the letter D, indicating that the file has been deleted from the database. The blue flag is on the first line because is the best full least-squares fit of the possible records. It is noted that all first solutions are 'Celestine', because this mineral appears repeatedly in the database.

It can select (or discard) the crystalline phases identified correctly by ticking the appropriate box, or pressing the keyboard space on the active line. You can also use the Del key to remove lines and keys Up , Down , Page Up , Page down , Home and End to move on it.

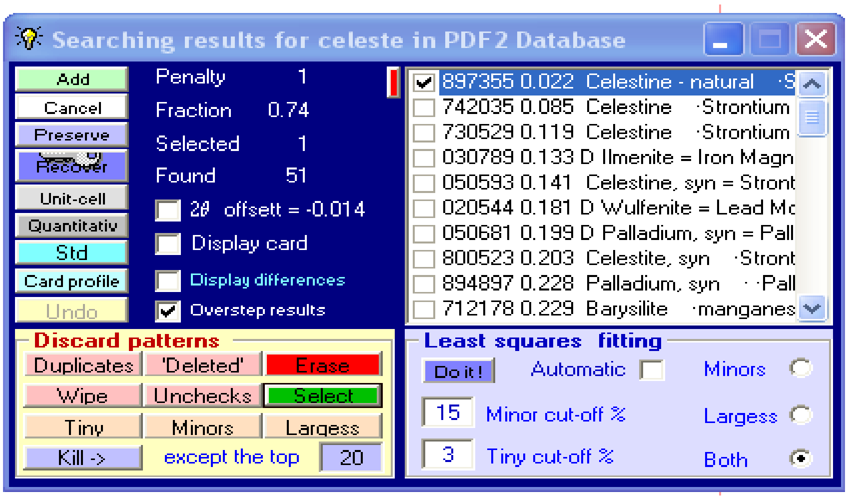


Figure 5.2. 'Matching' tool. Results with PDF2 database. (Please see updates Chapter)

To avoid the recurrence of similar results, ticking into the box Skip results , as explained in Chapter 2, figure 2.1. In this case, the best solution is shown as in Figure 5.3, where the mineral '*Celestine*' appears only once.

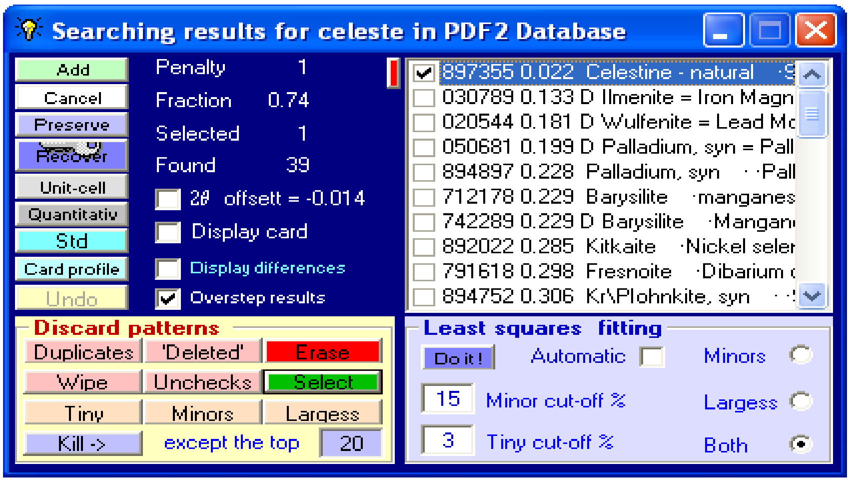


Figure 5.3. The box Skip duplicates was ticked in advanced searching options.

The remaining suggested phases (D Bopurnonite, etc.) have an excessive hyperdistance, so it will be to select as the most likely phase "Celestine" (box is marked √). To discard the rest has been pressing Uncheck).

Similar results can be obtained with the database AMSCD, which displays the list this time with blue color (Figure 5.4).

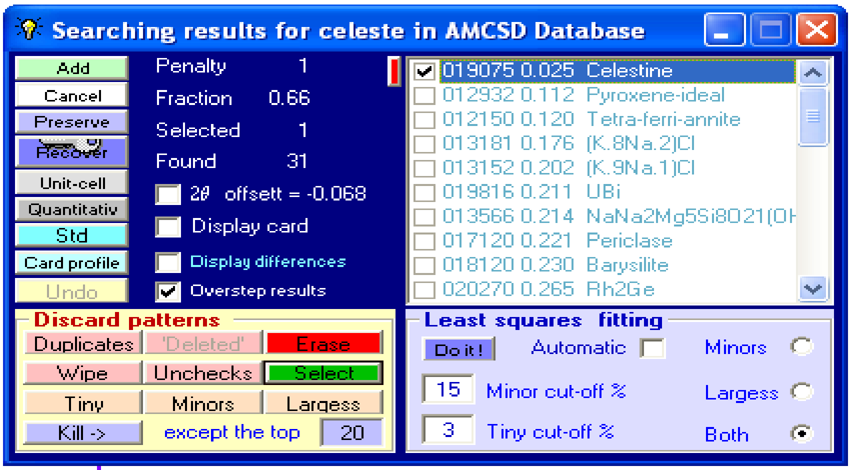


Figure 5.4. Results obtained from the database AMSCD. The Skip duplicates box is unchecked.

By clicking on any of the lines of the list, with shades of gray, a graphic overlay of the active record on the graphic pattern is made. If on the main screen ticked the K Alpha1-2 pointer box also shows the positions of the bars for Kα_2. If, moreover, K Beta pointer is marked, are shown in orange clear the positions of the bars Kβ.

In polimineric samples is the same way, but the list of suggested phases includes incorrect solutions and it should be analyzed using the '*matching*' tool. The example of the Figures 5.5 and 5.6 shows qualitative analysis of a sample with four mineral components (etc.) on the subfile 'Minerals' of PDF2, without taking into account 'Deleted' cards and Skip duplicates with the option selected.

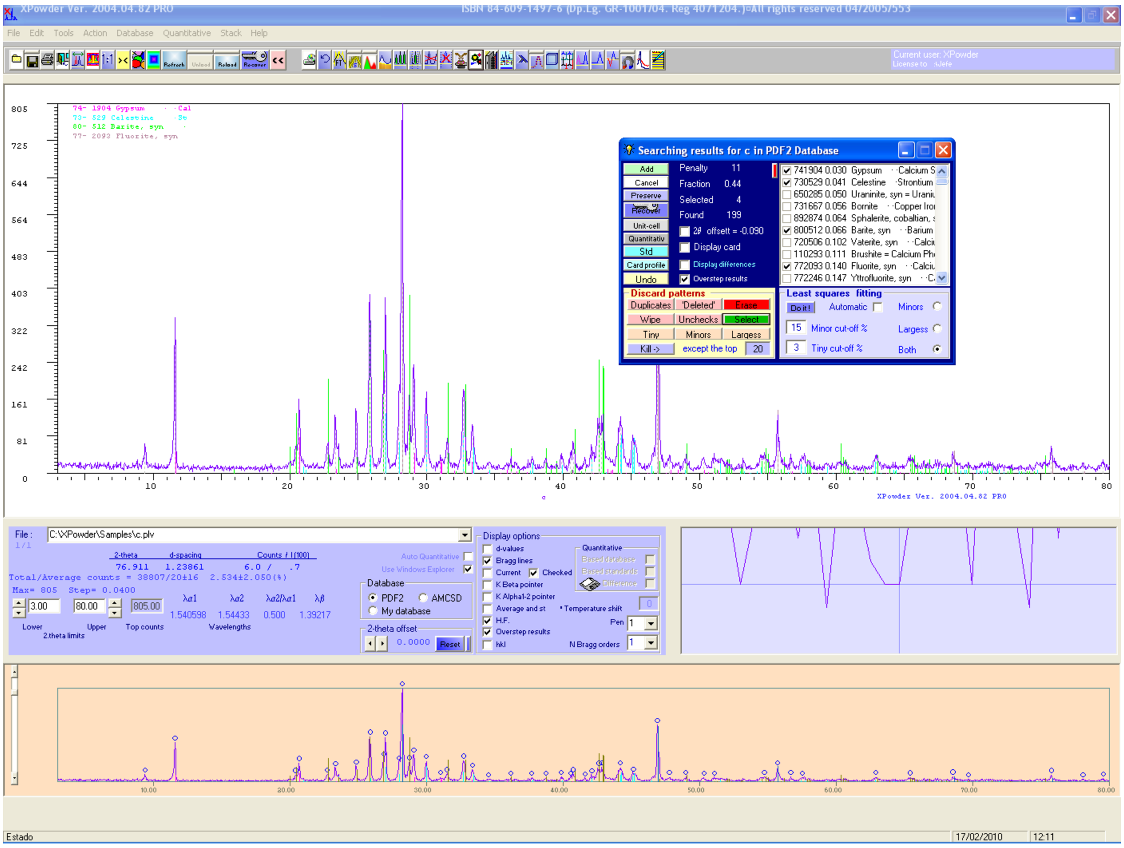


Figure 5.5

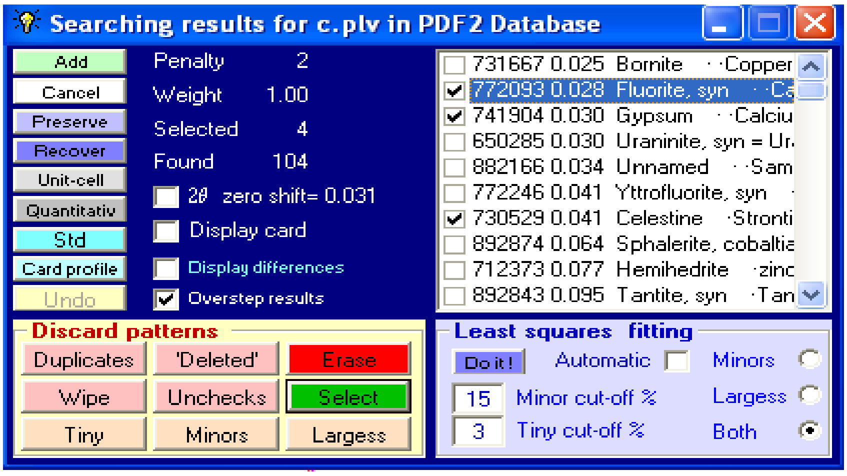


Figure 5.6.

Figure 5.7 shows the result list. It is noted that the phase with lesser Euclidean hyperdistance (0,025 bornite) does not match the one that best fits by least squares (0,028 Fluorite syn). It is for the user decides which ones are the most appropriate allocations. In this case, and given that some phases can be identified really isostructural terms of those obtained after a detailed analysis with this tool we reach the conclusion that these are shown in Figure 5.8. To be ticked the Checked box, the bar charts of the database, automatically weighted, overlapped with the original using color codes. To stop the cursor on reflection, they show the rates of the reflections of each component (box with a yellow background on 2θ=26º in Figure 5.6).

In addition to '*Set*', '*File*' and hyperdistance, the tool '*Matching*' figure of 5.6 contains the following messages:

Penalty: Order on the list according to the hyperdistance.

Weight: It varies between 0 and 1. Is the fraction of heavy intensities of the database record that best fits the experimental.

Selected: Number of cards accepted and marked (√). The maximum value is 11.

Found: Number of phases suggested during 'searching'.

'Matching' commands (Figure 5.5.)

Add. It allows you to add to the list new results through new qualitative analysis.

Cancel. Rejects all the results and hide the tool.

Preserve. Saves the current results, which could be recovered, to be charged the same diffractogram subsequently, through the order Recover. Both orders appear repeatedly in other parts of the program. It also can be retrieved at any time from the menu on the homepage (for example to contrast or implement the results of this sample other of the same nature):

File -> Mi favorite compounds

Unit-cell Lets unit-cell refinement of the crystalline phase corresponding to the actual card, both automatic or controlled way. (Horizontal blue flag in Figure 5.6). (See Chapter 9).

Quantitativ. It allows the non linear least squares quantitative analysis for of the phases identified including statistical and global amorphous stuff, overall from the database records. The program takes chemical composition and density from the database in order to calculate the linear mass absorption coefficients. If these data are not present in the database, the program assigns

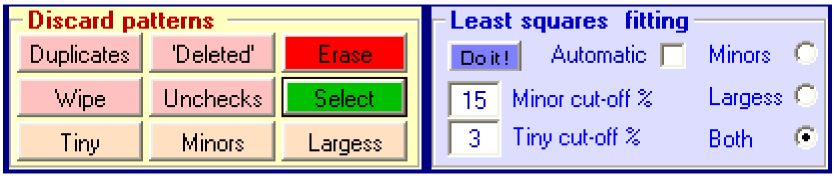
approximate coefficients. The overall mass absorption coefficient of the sample is calculated during the process. The program assigns the RIR factor (*Reference Intensity Ratio*) value of the card in the database. PDF2 use in this sense the coefficient 'I/Icor', which is usually wrong in most cases, as documented by the fact that there are numerous examples in which a single crystalline phase shows variations of up to an order of magnitude in the same database (for example, a mineral composition as invariant as is the quartz 'I / Icor' ranges from 2 to 20, leading to errors of up to 50% by weight and even mayors). Other times this factor is not included in some chips from the database. In conclusion, to ensure proper quantification each investigator must use their own values of the RIR coefficients. The best way to calculate it is through registration Diffractometer setting of a 'pure pattern' of each substance to quantify, 50% mixed and homogenized with another 'standard reference' stable (as far as possible and crystallinity homogeneous mass absorption coefficient similar to set of mixing problem). This often sometimes unlikely. The Corundum or synthetic (Al_2O_3) powder are often used as standard reference, after being passed through a 20 μm sieve. The RIR factor is calculated by dividing the maximum intensity of the reflection phase of the pattern pure by the intensity of the reflection maximum of corundum. But it is much better, though more laborious, making the ratio of the integrated intensities of all reflections of each phase. More details on the quantitative analysis are shown in Chapter 6.

Std It incorporates the record to the list of standard patterns (text file 'std.txt').

Card profile Allows the estimated diffractogram of the actual card for the active database (horizontal blue flag) in accordance with the standard profile of lines and Caglioti equation (see Chapter 10). Not included in calculating the asymmetry of the peaks, but if the box $K\alpha_2$ and, or, $K\beta$ are activated in the initial screen, the corresponding profiles are calculated. Subsequently, the profile can be calculated subtracted from the original diagram. The latter can be used to highlight the remaining components of the experimental diffractogram residual. The asymmetry of the peaks is not included in the calculation, but if case of the $K\alpha_2$ and, or, $K\beta$ boxes are activated in the main screen, the corresponding profiles are calculated. Subsequently, the calculated profile can be subtracted from the experimental pattern.

Undo It let recover the last database pattern erased by Erase .

Within the framework **Discard pattern** are buttons that enable solutions to eliminate recurring patterns (Duplicates) , PDF2 'deleted' patterns ('Deleted') or a particular solution (Erase). This last, clears the list of the active row (horizontal blue flag). Can be replaced by the key Del of keyboard.



Wipe Discard all results from the list.

Unchecks. Erase all the results from the list that have not been marked. Can be replaced by the Esc keyboard.

Select It let select the actual pattern on the list. It is equal to clicking on the box ☑ of the pattern list. Can be replaced by the Espace keyboard.

Tiny Minors Largess They eliminate respectivelly the tyni, minors and largess components according to values into the boxes Tiny cut-off 5 y Minor cut-off %

Do it ! Perform least squares fitting of better database pattern of list according to the selected button option (Minors, Largues o Both) . This button is unable in the case of Automatic is checked.

Others options:

Launching "MyDatabase.Myd" (**See also update 2010.01.10**)

Following commands are used:

(Main menu). Write the actual experiemtal Bragg reflections in a new record in 'Mydatabas.MyD' (fig. 5.7)

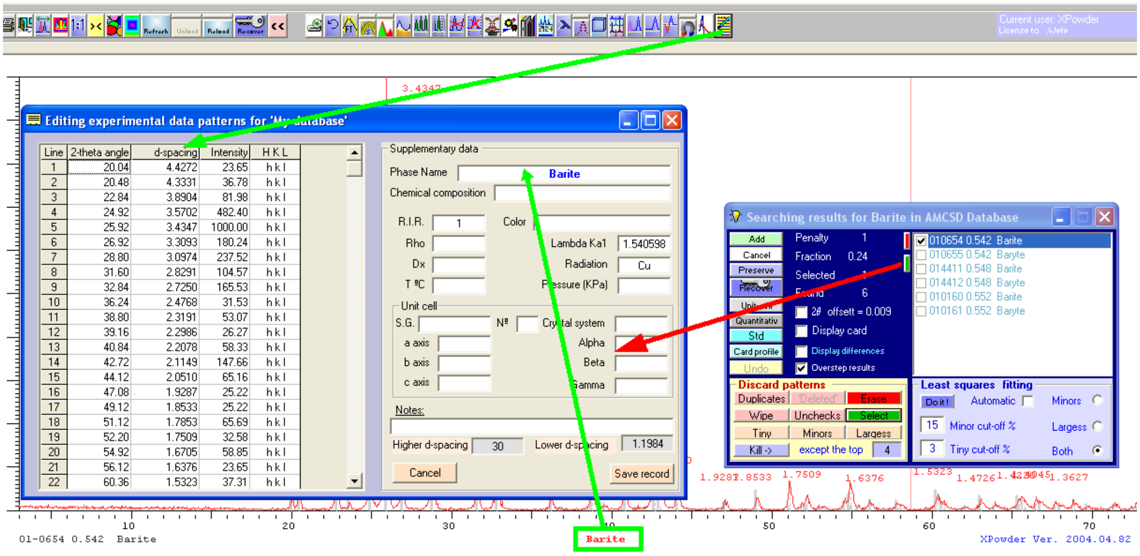


Fig 5.7

Exports the crystallographic data of active database (no reflections) to the new experimental record file (Figure 5.8, data in red). This data can be edited before finally being recorded in 'Mydatabase.MyD' with the order Save record

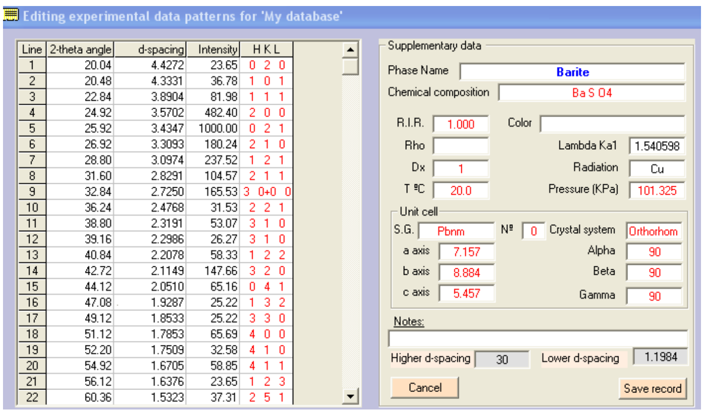


Fig 5.8

Export directly the actual record of the active database to 'Mydatabas.MyD'.

The first pattern of "mydatabase" should be created with a diffractogram of our own laboratory diffraction. Thus, the experimental model for the rest of the database will be related to it.

Display card. When marked, the database record appears on a floating screen (Figure 5.7).

Anothers options :

zero shift= -0.007 When marked, check the database record and corrects original 2θ error scroll (-0.007 in the example). Corrected values are graphically displayed on the main screen (*matching*).

Display card. When checked, the main features of database pattern are displayed (figure 5.7).

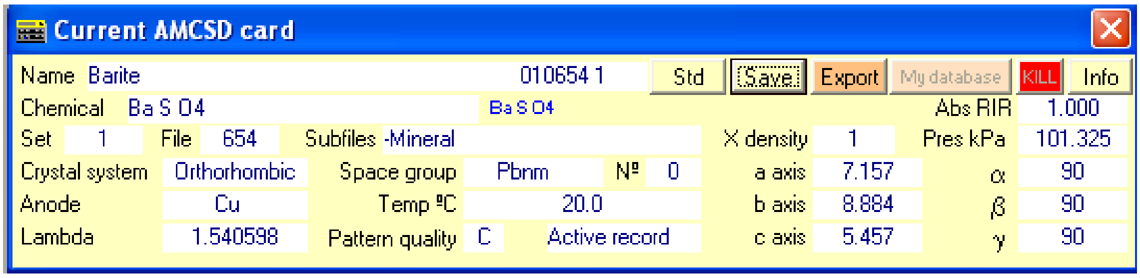


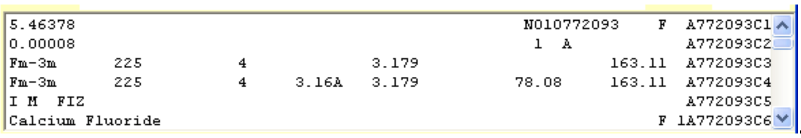
Figure 5.7.

Export Equal to

Std It incorporates the record to the list of standard patterns of the program (text file 'std.txt'). It is equal to Std of figure 5.6.

Save It creates the file 'Card.txt' with the actual data record information in the directory of the program.

Info Displays the full content of the original database record:



Display differences When checked, and click the button Card profile , the difference diffractogram between the experimental and calculated patterns is drawn.

Overstep results When marked, the results list will apply to all diffractograms loaded. This option can be also selected on the main screen.

Home

Chapter 6. Quantitative analysis by RIR (*Reference Intensity Ratios*) methods.

Preliminary: The phase quantification by X-ray powder diffraction methods is a complex process due to factors that mainly depends on dealing methods used in the diverse laboratories. Factors such the alignment difractometer, type of slits, linearity in the response of radiation counters , uniformity in the size of grains of the sample, orientation linked to how to prepare the sample or the habits, etc make many published results are of an error greater than the one intended. Spectacularly wrong can be some results based on the measurement of the intensity of a single reflection corrected by factors of proportionality, in some cases obtained by different laboratories to own or taken from literature ('*Easy quantitative Analysis*'). Other more sophisticated methods, including the Rietveld method, can provide more precise solutions, but require an exquisite care in sample preparation, registration and in parameterization of diffractogram models, both instrumental and structural components. XPowder uses non-linear least square methods for full diffractogram opposite of a weighted combination of diffraction diagrams taken directly from the database (another method that will explain later -Chapter 7- is based on adjustment for diagrams Experimental patterns). It was subsequently corrected, within the possibilities it raises awareness of the pure phases, factors such as components and amorphous absorption. The same definition of 'component amorphous global' (Global Amorphous Stuff) should be taken in any case as an approximation to a reality that is described with difficulty. By using all reflections of each component makes it minimizes effects such as the preference orientation, but there is no doubt that not just the problem completely. So it is desirable, select those standard cards that fit the diffractograms, among the possible solutions found identical. It is very interesting in this sense to use the option 'Skip duplicates', as the program adjusts the best database records among identical results. No less important is the election of appropriate RIR factors because they involved directly % weighting of each phase. Finally XPowder indicated that performs the calculations properly, according to well-established methods in general treaties of Statistics and Crystallography, so the quality of the final quantifications depends only on the modes of operation of each user.

Beginning with the 2004.3.1 update, XPowder incorporated into the professional versions a powerful tool that allows precise quantitative studies done by methods of nonlinear least squares on a full profile of the full diffratogram and that takes full advantage of the information contained in the database records. The analysis can be conducted on a isolated specimen or groups of up to 50 samples simultaneously. The weighting is achieved with the standard method RIR (Normalized RIR Method), described by Chung (1974: "Quantitative interpretation of X-ray diffraction patterns. I. Matrix flushing method of quantitative multicomponent analisys. Jour. Pf Applied Crystallography, v.7 , 519-525). Another method much more accurate quantification will be explained in Chapter 7.

Although the initial versions, the amorphous components were excluded from this quantitative analysis, the program XPowder has the ability to generate a pseudo-RIR factor for the Global Amorphous Stuff that is optimized for each type of overall chemical composition, so that the program uses the 'experience' of previous analysis and optimizes the ratios as an 'historic' (this must be taken into account in cases where the program optimizes your values in the midst of an experiment in quantitative analysis, in which case it is recommended repeat all the calculations made in the same session). The pseudo-factor of amorphous RIR is calculated from statistics that include the standard deviation of the full accounts of the diffractogram and the relationship of 'accounts crystalline / background accounts', from an initial value definable preferably in each lab. The results of analysis of amorphous are more valid in terms of analyzing samples of similar composition. The results are better when amorphous samples are similar composition. The results are invalid in any case when the crystalline composition is incorrect. Complementary uses the 'Absorption-Diffraction Method' that involves calculating the *absorption mass coefficients* of each component and the total sample. The latter is calculated on the composition of the departure from the standard method RIR. The automatic use of these methods assumes that the database contains the chemical composition of each phase. In other cases XPowder provisional values assigned to the parameters m / r, which can be modified by the user. The composition (C_i) of the component (i) is obtained in the mixture (s) from the fraction of the mix function (X_i) of each partial diffractogram, which is obtained by non-linear method of least squares (Heavy optional) on the full profile:

$$C_i = X_i \, (\mu/\rho)_i / (\mu/\rho)_s$$

2θ instrumental deviations optionally can be corrected during the refinement process.

The procedure that the user should be further simplified to the maximum, because it is not necessary to sample preparation patterns or the construction of curves and abacus for obtaining the weight percentages. The only requirement is that the database records used in the evaluation include information on the chemical composition and value of the RIR (*Reference Intensity Ratios*), which is customary in the latest versions of *PDF2*, but are not included in the database *DifData-AMSCD* database. In another case, these values can be added by the user with data measured in the laboratory or estimated from samples of known composition. The quality of the results is generally good and depends only on the quality of the diffractogram, the database patterns, the value of the RIR and its universality. It is always preferable to use mixes of patterns and corundum with particle size of 20 μm to about 50% by weight and measure own RIR values.

The protocolose shown in the following example (corresponding to the sample C. PLV of the sub-directory \ EXAMPLES that is installed with the program):

1. We must never subtract background (this will differ in recent versions of the program of previous ones).
2. It should be read automatically or manually peaks of the diffractogram pattern in order to calculate the d-spacing of the most accurate manner.

3. We have to make a correct identification of crystalline phases and select them ☑ in the window *Results* of tool '*Matching*' (see Chapter 5, Figure 5.7 and 5.8).

4. We must come to the window of quantitative analysis (Fig. 6). This can be done from the tool 'Matching' (Quantitativ) or from any other part of the program (for example, Menu on the main page -> Quantitative -> LS RIR Database cards).

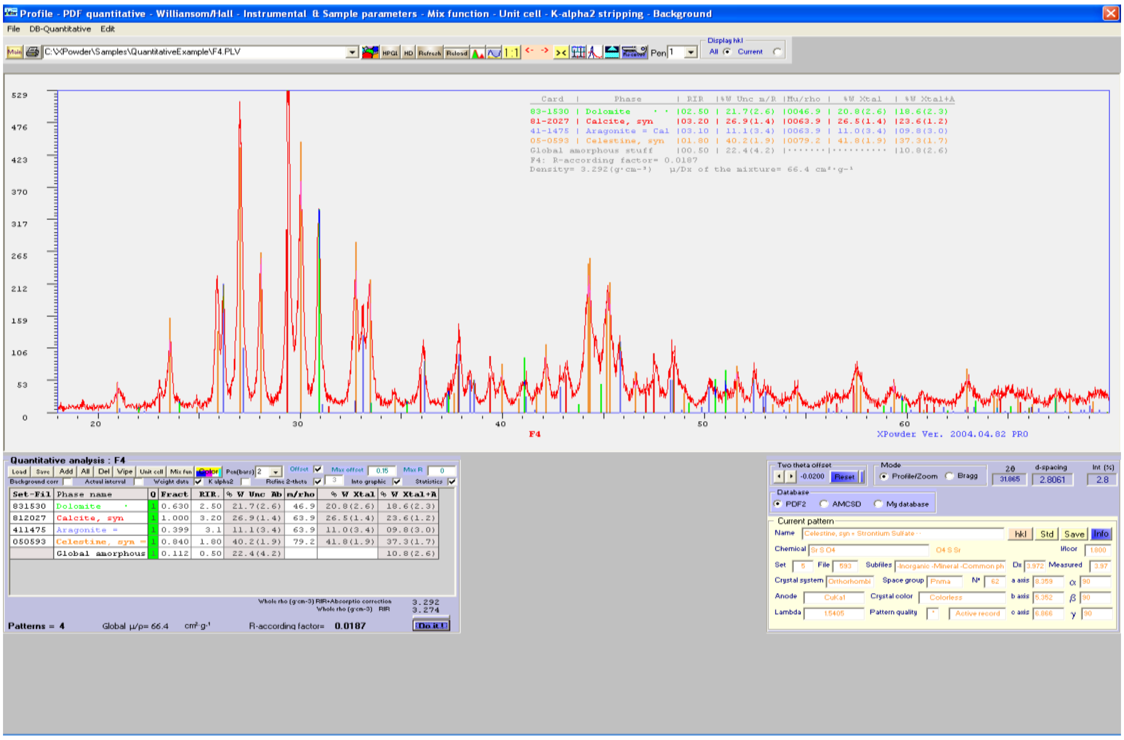


Figure 6.1.

5. The tool of quantitative analysis appears as in Figure 6.2, showing the previous results obtained directly from the parameters that the program has a default. RIR and μ/ρ RIR values are calculated and incorporated automatically from the content of the database. If any of these records is not the factor I/ICor, the program assigns a provisional 1. Subsequently can be changed by the user to appropriate values, obtained in the laboratory or from literature. The lack of data density and chemical composition is also approach by the program.

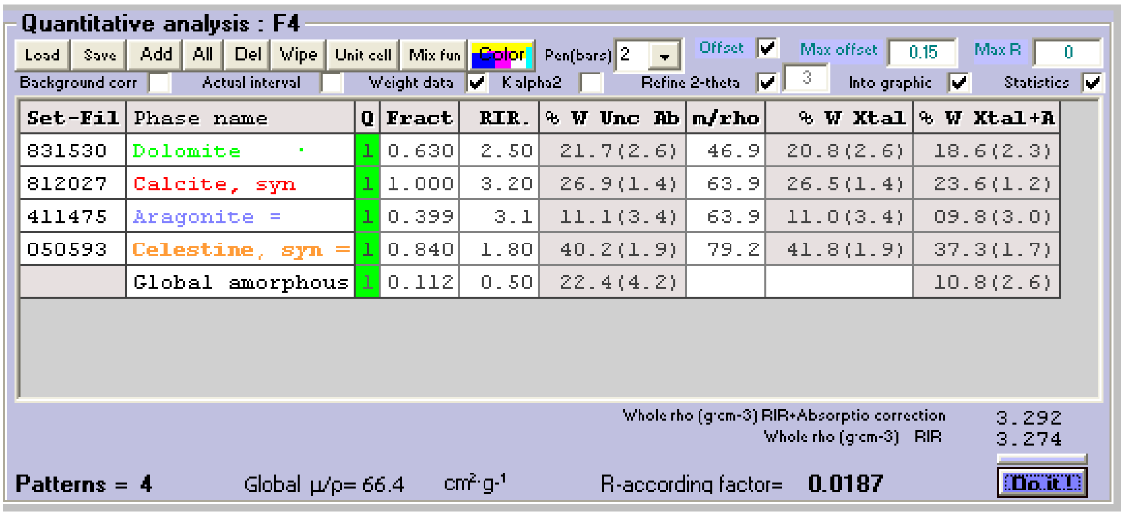


Figure 6.2.

In any case, you can always modify the values of the parameters RIR and μ/ρ for each type of composition (including the amorphous pseudo-RIR value) and recalculate the quantitative by pressing 

. Right part of this button performs the simultaneous analysis of all the loaded in computer memory diffractograms (50 maximum). All data are collected in the archive (logfile.tmp) that can be saved at any time from the menu "File-> Save Log File as TXT".

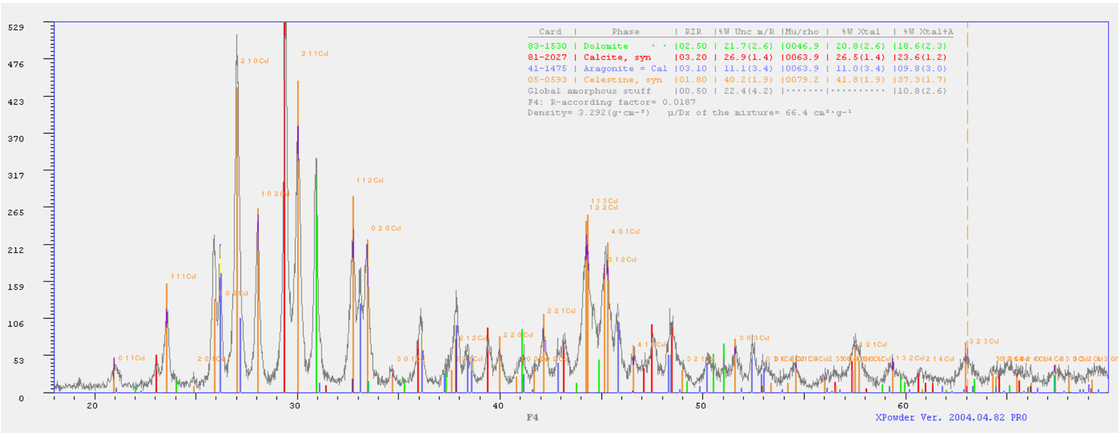
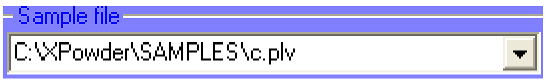


Figure 6.3.

<u>Description of the RIR tool</u> (Figure 6.2.)



This is the file of the active diffractogram. Can be changed by clicking  in the text box.

By checking the boxes are made respectively the following:

- It takes in account the background in according factor calculation
- Adjust the analysis to the current range of 2θ.
- The experimental data are weighed according to **w = 1/√Counts**
- $K\alpha_2$ 2 is included in the calculation of the profile function and the graphics (does not affect the quantitative analysis).
- The D-space values of the database patterns are refined
- Statictis are Included 'Log file' and graphical output.

If checked, 2θ experimental pattern offset is refined. Maximun 2θ offset must be = Max offset value. According R for convergence is Max R.

R-according factor= **0.0187** It is defined as::

$$R= \mathbf{\Sigma} \{ w(I_O - I_C) \mathbf{/ \Sigma} wI_O$$

To obtain good values of R is necessary to use those cards in the database whose intensities best fit our experimental diffractograms. The best results are obtained with their own records (mydatabase).

Set-Fil	Phase name	Q	Fract	RIR.	% W Unc Ab	m/rho	% W Xtal	% W Xtal+A
831530	Dolomite ·	1	0.630	2.50	21.7(2.6)	46.9	20.8(2.6)	18.6(2.3)
812027	Calcite. syn	1	1.000	3.20	26.9(1.4)	63.9	26.5(1.4)	23.6(1.2)

Head of quantitative table of active experimental pattern. First column = Set (two digits) and file (four digits). Second column =phase name. Third column=(1) if phase will be quantified, and 0 for no analysis. 'Fract' column shows L.S. fractional composition of reference phase (0 to 1. 'RIR' similar to '*Reference Intensity Ratio*' of phase reference, for all experimental pattern. Must be experimentally measured and can be edited and saved.'% W Unc Ab' % weight uncorrected for absorption. 'mu/rho' masic absorption coefficient calculated from chemical and density values of database record. % W Xtal column shows % weight (Sum= 100%) of crystalline components. Last columns is equal from previous but includes estimated Global Amorphous Stuff % (GAS), obtained by:

$$GAS= \left\{ \left[(\mathbf{\Sigma}\, \mathbf{I}_i\,) / N\right]^2 + \sigma^2 \right\}^{1/2}$$

Where: $\mathbf{I}$ is diffracted intensity in the point **i** . N = Number of measured points in X-Ray pattern. $\sigma = \mathbf{I_i}$ standard deviation.

The non-linearity of the GAS factor value is corrected by using mixtures with known contents of amorphous (glass in our case), and fit with a polynomial. For a Bragg-Brentano configuration, automatic slit and CuKα radiation and 2nd monochromator we can use the 5th grade polynomial:

$$^{True}GAS = -25.8483 +3.7592\cdot X+ 0.6203\cdot X^2 -0.0535\cdot X^3 \;\; 0.0016\cdot X^4 \;\; -0.000016\cdot X^5$$

Where X= GAS calculated from above formula. To perform linear correction is necessary to include an instruction on the '**XPowder.ini** file, containing the list of the polynomial coefficients:

Amorphous_Polynomia_Coef = 0 1 (no polynomial correction).
Amorphous_Polynomia_Coef = -25.8483 3.7592 0.6203 -0.0535 0.0016 -0.000016 (for the 5th grade polynomial of the example).

RIR factors must be measured experimentally on the diffractogram of an artificial mixture, whose components are known weights. Among these components must have a stable pattern, common to all samples to be analyzed (quartz, fluorite, NaCl, corundum, CeO, B_6La, etc). After, a prior quantitative analysis is done with XPowder, using initial $\mathbf{RIR}_{phase}$ values equal to one. The final $\mathbf{RIR}_{phase}$ factors are determined for each component according to:

$$\mathbf{RIR}_{phase}= \left(\underline{\mathbf{\%\,W\,Xtal}}_{phase} / \underline{\mathbf{\%\,W\,Xtal}}_{\text{reference pattern}}\right) \cdot \left(\underline{\mathbf{Weight}_{(mg)}}_{\text{reference pattern}} / \underline{\mathbf{Weight}_{(mg)}}_{phase}\right)$$

The first two factors are obtained in the penultimate column of the output table of prior quantitative analysis and the latter two are the real weights of each component used to prepare the artificial sample. The calculated $\mathbf{RIR}_{phase}$ values can be then used in future analysis in order to obtain absolute percentage results. Note that only need to use an artificial mixture for each paragenesis.

Across the table shows the standard deviation in brackets after each outcome.

Tools Load | Save | Add | All | Del | Wipe | Unit cell | Mix fun | Color | Pen(bars) | 2

Load Allows loading specific configuration parameters for each type of samples or associations, that has been previously saved with Save. This latest order allows you to create specific configurations of usual samples.

Add It allows you to add manually database records to be weighted in the quantitative analysis. It is necessary to know before the reference (*Set* and *File*) of each record.

All Select, or discarded, alternately all database records from the list of quantitative analysis.

Wipe Clears the list.

Unit cell Unit-cell refinement using active reference phase pattern.

Mix fun The theoretical and difference patterns, based in the database cards, are calculated from the quantitative composition. The program uses the active profile parameters (Caglioti parameters and pseudo-Voigt average profile function). The calculation does not include asymmetric peaks, but the effects of the lack of monochromatism of the radiation.

Color 2 Allows you to select the color and size of the pen bar of the active database record (orange horizontal bar in the example in Figure 6.2) who is drawn in the diffractogram pattern graphic (Figure 6.3).

Do it! The program makes quantitative analysis with the current parameters are listed in the table (as in Figure 6.2). Right part of this button performs the simultaneous analysis of all the loaded diffractogram patterns in computer memory (50 maximum). All reulsts are collected in the archive (logfile.tmp) that can be saved at any time from the menu "File-> Save Log File as TXT". It is assumed that they all have the same qualitative composition, although it admits that some component has zero % in composition), as shown in the 'log file' example:

```
--------------------------------------------------------------------------
Quantitative section based on PDF2 cards
Sample= C:\XPowder\SAMPLES\A.plv
  Card  |       Phase       | RIR  ·  %Weigth  |Mu/rho ·        %Weight
---------------------------------------------------------------------------
77-2093 | Fluorite, syn   |03.80 · 01.9(0.6) |0115.2 · 01.8(0.8) |01.8(0.8)
77-1904 | Gypsum     · ·Ca |01.70 · 02.1(0.6) |0060.8 · 01.8(0.8) |01.8(0.8)
77-0529 | Celestine    ·   |01.90 · 26.5(0.8) |0082.6 · 24.7(1.0) |24.6(1.0)
77-1378 | Barite     · ·Ba |02.80 · 69.5(9.4) |0286.4 · 71.7(7.7) |71.4(7.7)
Global amorphous stuff    |00.55 ············|···················|00.4·····
A.plv: R-according factor= 0.0274
Density= 4.281(g·cm-³)   µ/Dx of the mixture= 224.3 cm²·g-¹
Sample= C:\XPowder\SAMPLES\B.PLV
  Card  |       Phase       | RIR  ·  %Weigth  |Mu/rho ·        %Weight
---------------------------------------------------------------------------
77-2093 | Fluorite, syn   |03.80 · 15.2(1.7) |0115.2 · 14.9(1.7) |14.8(1.7)
77-1904 | Gypsum     · ·Ca |01.70 · 15.9(0.6) |0060.8 · 14.3(0.8) |14.3(0.8)
77-0529 | Celestine    ·   |01.90 · 32.5(1.4) |0082.6 · 31.5(1.4) |31.4(1.4)
77-1378 | Barite     · ·Ba |02.80 · 36.5(7.6) |0286.4 · 39.3(6.3) |39.2(6.3)
Global amorphous stuff    |00.55 ············|···················|00.4·····
B.PLV: R-according factor= 0.0303
Density= 3.808(g·cm-³)   µ/Dx of the mixture= 158.4 cm²·g-¹
Sample= C:\XPowder\SAMPLES\c.plv
  Card  |       Phase       | RIR  ·  %Weigth  |Mu/rho ·        %Weight
---------------------------------------------------------------------------
77-2093 | Fluorite, syn   |03.80 · 30.8(8.4) |0115.2 · 31.0(7.0) |30.8(6.9)
77-1904 | Gypsum     · ·Ca |01.70 · 24.7(0.7) |0060.8 · 22.8(0.9) |22.7(0.9)
77-0529 | Celestine    ·   |01.90 · 27.4(1.3) |0082.6 · 27.3(1.4) |27.1(1.3)
77-1378 | Barite     · ·Ba |02.80 · 17.1(0.9) |0286.4 · 18.9(1.0) |18.8(1.0)
Global amorphous stuff    |00.55 ············|···················|00.5·····
c.plv: R-according factor= 0.0207
Density= 3.439(g·cm-³)   µ/Dx of the mixture= 122.0 cm²·g-¹
Sample= C:\XPowder\SAMPLES\D.plv
  Card  |       Phase       | RIR  ·  %Weigth  |Mu/rho ·        %Weight
```

```
------------------------------------------------------------------------------
77-2093 | Fluorite, syn   |03.80 · 13.0(1.9) |0115.2 · 12.7(1.8) |12.6(1.8)
77-1904 | Gypsum      · ·Ca |01.70 · 16.8(0.6) |0060.8 · 15.1(0.8) |15.0(0.8)
77-0529 | Celestine     ·   |01.90 · 33.0(1.5) |0082.6 · 32.0(1.5) |31.8(1.4)
77-1378 | Barite      · ·Ba |02.80 · 37.3(7.4) |0286.4 · 40.2(6.2) |39.9(6.1)
Global amorphous stuff    |00.55 ············|···················|00.6·····
D.plv: R-according factor= 0.0263
Density= 3.817(g·cm-³)   µ/Dx of the mixture= 159.2 cm²·g-¹

Summary of quantitative analysis of crystalline components
-----------------------------------------------------------------------------------
Sample              Fluorite, Gypsum    Celestine  Barite     R-acc   Densit C.Mas
A.plv               01.8(0.8) 01.8(0.8) 24.7(1.0)  71.7(7.7)  0.0274  4.281  224.3
B.PLV               14.9(1.7) 14.3(0.8) 31.5(1.4)  39.3(6.3)  0.0303  3.808  158.4
c.plv               31.0(7.0) 22.8(0.9) 27.3(1.4)  18.9(1.0)  0.0207  3.439  122.0
D.plv               12.7(1.8) 15.1(0.8) 32.0(1.5)  40.2(6.2)  0.0263  3.817  159.2

Summary of quantitative analysis of crystalline compounds and amorphous stuff
-----------------------------------------------------------------------------------
Sample              Fluorite, Gypsum    Celestine  Barite     Amorp R-acc  Densit C.Mas
A.plv               01.8(0.8) 01.8(0.8) 24.6(1.0)  71.4(7.7)  00.4 0.0274  4.281  224.3
B.PLV               14.8(1.7) 14.3(0.8) 31.4(1.4)  39.2(6.3)  00.4 0.0303  3.808  158.4
c.plv               30.8(6.9) 22.7(0.9) 27.1(1.3)  18.8(1.0)  00.5 0.0207  3.439  122.0
D.plv               12.6(1.8) 15.0(0.8) 31.8(1.4)  39.9(6.1)  00.6 0.0263  3.817  159.2
End Quantitative section
-----------------------------------------------------------------------------------
```

In addition to the tool of estimate quantitative, a table is shown with the active database card (Fig. 6.4).

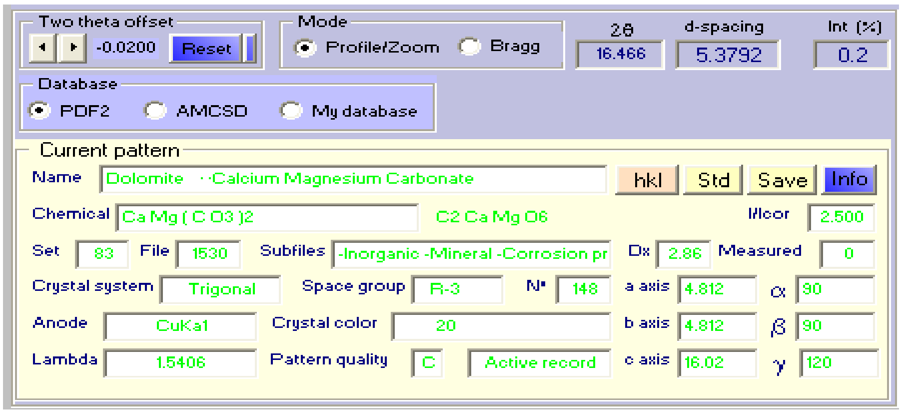
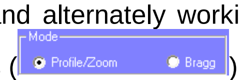
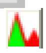


Figure 6.4.

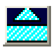
This card is very similar to that described in Chapter 5 (Fig. 5.9). It also added to the pattern graphic hkl indices of the identified phases (Fig. 6.3) with the button hkl, manually correct the 2θ error and alternately working in mode 'Profile Analysis (Chapter 8), or edit mode Bragg´s reflections ()

Auxiliary buttons

The first nine buttons have the same significance as in other parts of the program. They are important on this page  ($K\alpha_2$ stripping) and  background subtraction).

<- -> Move the diffractogram pattern to the right or the left.

>< Decreases the zoom level.

 Performs analysis profile of reflection marked with the left mouse button.

Choose which **hkl** index are shown on screen when it stops the cursor on the graphic pattern.

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Chapter 7. Quantitative analysis using experimental standards.

This is the most accurate way to quantify phases through X-Ray diffraction by the powder method. However requires a careful handling of samples, both of which are used as standard as those that are analyzed.

The method requires the record of diffraction patterns of pure crystalline compounds with the same composition and similar crystallinity to those present in the speciment. When the quantitative analysis is performed, the program makes an adjustment for non-linear least squares to find the mix of diffractogram standard patterns to the experimental pattern.

If the crystallinity among the specimens and standard patterns are very different, it is desirable to make records with different crystallinity patterns. The program will make the weighting of each of them, as if they were separate phases. May also be included diffractograms of amorphous substances for global quantification of them in the analyzed mixtures. The use of internal standards of known weight (eg 10% of corundum Al_2O_3) allows absolute quantitative analysis.

During the analysis the 2θ displacement and the mass absorption coefficient are refined. Data must be statistically weighted.

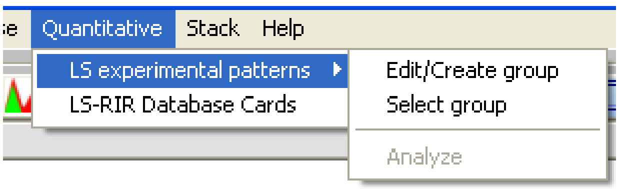
Once obtained the diffractograms standard patterns, it is easy for serialized quantitative analysis with a precision that is generally higher than those obtained by Rietveld methods or RIR-database based correction.

The quantitative analysis are more accurate when made with care the following:

- The volume of standard sample and specimen used in all registrations should be the same. An minimum % of Internal standard compound can be artificially added to the specimen.
- The pressure of compaction of crystalline powder should also be similar.
- It is necessary to use a stable sample pattern to control the derive of the X-Ray meter. The best thing is to use is a pressed tablet having similar absorption coefficient which samples to be analyzed, wherever possible.
- The same radiation, monocromatization system, set of slits, detector and values of discrimination of the detector should be used forever.
- The diffractograms of the tablet pattern and the standard patterns should preferably be in the same session.
- Where then is necessary to create new standard patterns, must be measured also shows stable tablet pattern, in order to correct derive or decay.
- The historic change of intensity is corrected by a factor, which is the ratio between the two measures (I_{old}/I_{new}). To this value, you can use a single reflection, or rather the cumulative intensity of several reflections and even entire diffractogram.
- Exceptionally, they can be used calculated diffractograms from the crystal structure, through programs such as Cerius, Mercury, etc., whenever possible to normalize the intensity by a appropriate factor.

Access to such analysis is done from the main menu with the command:

Quantitative -> SL Experimental Patterns



There are three subcommands ('Edit/Create group', 'Select group' and 'Analyze'), which will be as follows:

Edit/Create group

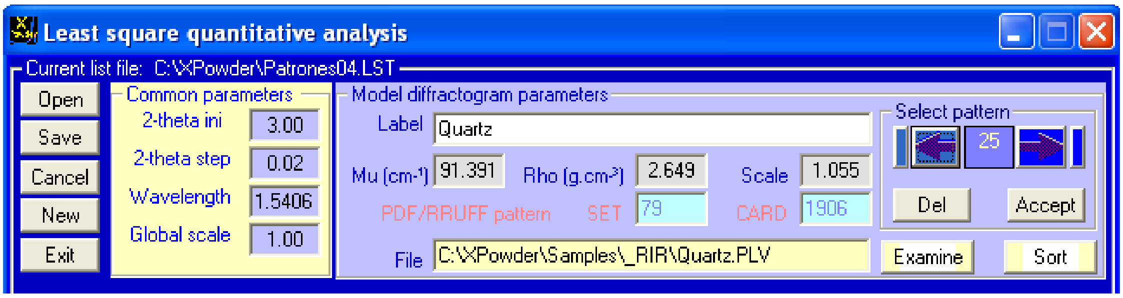


Figure 7.1.

Open To open and edit a previously created file that contains group of crystalline and, or, amorphous phases. These files are text format ('ascii') and the extension '. LST'
Save It allows to save a group phases for later reuse with Open .
Cancel Return without any operation.
New Lets create a new group.
Exit Return to the main screen, after requiring the recording of the group created.
Del Erase data from the active compound whose order number appears in the box under the message ' Select compound'.
Accept Accepts the selected pattern. Equivalent of pressing the right arrow.
Examine Lets explore the computer disk drives to locate the file of the standard substances (Barite.PLV in the example). When you load the file, the boxes Label , File and Common parameters are filled automatically. These should be identical for all phases listed. The figure Global scale is 1 normally but can be modified with the same approach that the term Scale,, as shown in the following paragraph. All the boxes may be edited, but 2-theta ini, 2-theta step y and Wavelength must coincide with those of the corresponding specimen diffractogram patterns.

The values of *lineal absorption coefficient* Mu(cm^{-1}), *density* Rho($g \cdot cm^{-3}$) , SET and CARD are optional, and should be entered manually. If the first two are not introduced, is not performed the absorption correction. CARD and SET are used to superimpose the reflection graph bars of the database records. The value of box Scale is 1 normally. Must be modified if the search pattern has been made after observing a variation of the intensities of the tablet standard sample with respect to other historical patterns used in the same association.

The left and right arrows (framework Select compound) let go through the list of patterns, or introduce a new one.

Figure 7.1 shows, for example, the fourth compounds (number 25 in the Select compound frame) for a association which includes all the possible data.

Select group

Lets explore the disks from the computer to select a file (.LST) created with 'Edit / Creat group'. Once loaded, the same group can be invoked repeatedly by using the Analyze menu or the button  on the main screen.

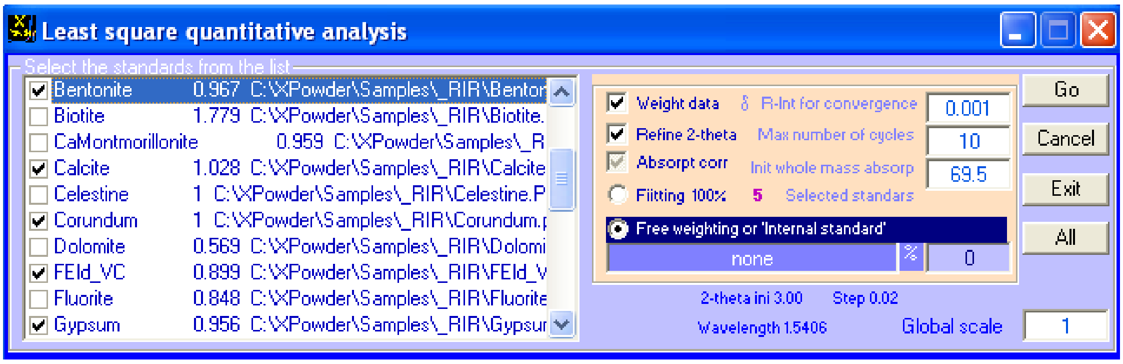


Figure 7.2.

The list on the left shows the components of the association and the files it contains diffractograms standard patterns. You can select (☑) part or all components of the list (Order All). If you have entered the values of the absorption coefficients and densities, you can tick Absorpt corr. You can also refine the mistakes of shifting angles 2θ (Refine 2-theta). You can also weight the experimental data (check box Weight data).

Maximun number of cycles. Limits the number of least squares cycles.

δ R-Int for convergence When it reaches this divergence value , the analysis stops even have not been completed cycles. Smaller values provide more accurate results.
results.

Init whole mass absorp . Initial estimated mass absorption coefficient for the specimen. It can be manually modified.

Exit Lets leave the quantitative analysis.

Cancel. Cancel any operation, and leaves the quantitative analysis.

Go Makes quantitative analysis.

Analysis options: There are two different operating modes.

1. 

The sum of components are 100 % fitted.

2. 

In turn provides two options:

2.1. Without internal standard (Free weighting): If not selected any internal standard (none), diagram calculated will be fitted in accordance with the experimental, but the results have a relative nature, generally do not total 100 (Figure 7.3).

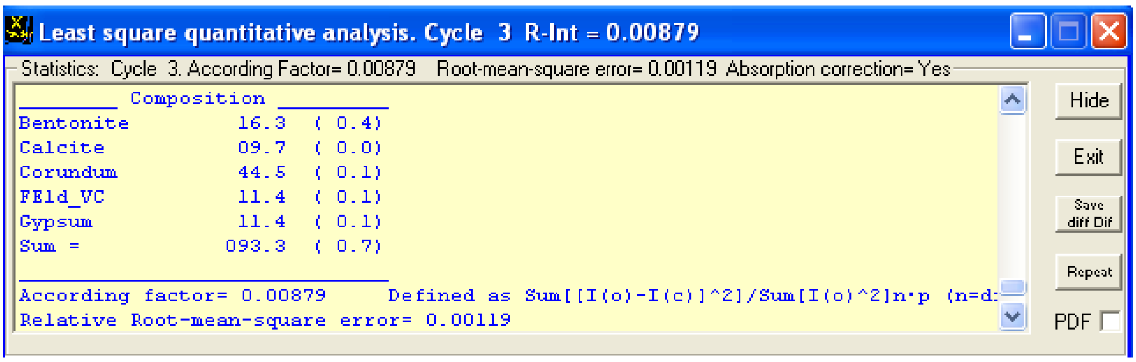


Figure 7.3

2.2. With internal standard. You can select from a list of components whose weight is known as internal standard (48% of corundum in the example of Figure 7.4). You can use a component of the mixture itself or added artificially.

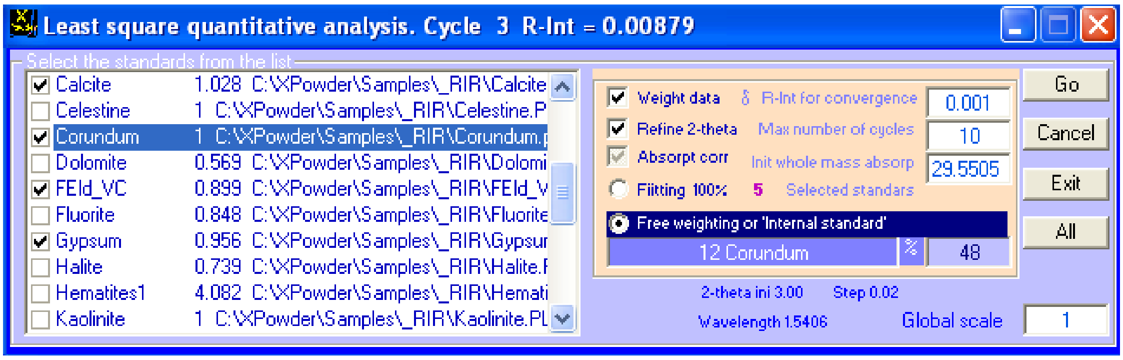


Figure 7.4.

To select the internal standard, you double-click on the appropriate line of the list (Corundum in the example), or on the box none . In the latter case the active compound is selected from the list. A new double-click on this box, discarding the internal standard. The quantitative composition (48% in the example) must be entered manually. The result of the analysis will be absolute in this case (Figure 7.5).

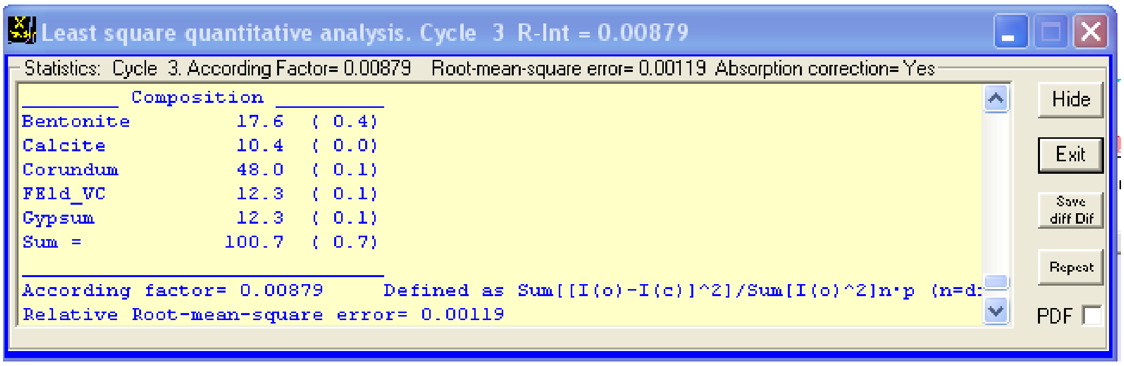


Figure 7.5.

The results (Figure 7.6) are displayed in the main graphic above and to the left. They include statistics and some auxiliary parameters obtained during the process. The calculated pattern (*mix function*) is shown with red dots overlapped by the diffractogram. The difference between standard and experimental diffractograms are shown in green at an height of close to 10% on the main screen and a 80% on the auxiliary lower pattern.

The header of the results screen (Fig. 7.5) shows the number of cycles performed before convergence, the factor of agreement, the mean square error final and informs us of the absorption correction.

The agreement factor (*According factor*) is defined as (2012.04.01 and later versions):

$$\textit{According Factor} = \left\{ {}_n\Sigma \left[w(I_o - I_c)^2 \right] / {}_n\Sigma\, w \left[I_o^2 \right] \right\} \cancel{n \cdot p}$$

where $\mathbf{I_o}$ are observed intensities and $\mathbf{I_c}$ calculated intensities. **n** = number of experimental points~~, p= number of standard patterns. n·p is constant for a each experience and it is used only for scale purposes.~~

Hide Minimizes the floating screen of figure 7.6. It's like you press the button -.

Exit Lets leave the analysis.

Save diff Dif Lets save the difference pattern in PLV format.

Repeat Lets repeat the analysis. The program leads to the figure 7.4.

PDF If you have filled the boxes SET and CARD (Fig. 7.2), and check the box PDF, the bar graphs of the database are displayed on the main screen.

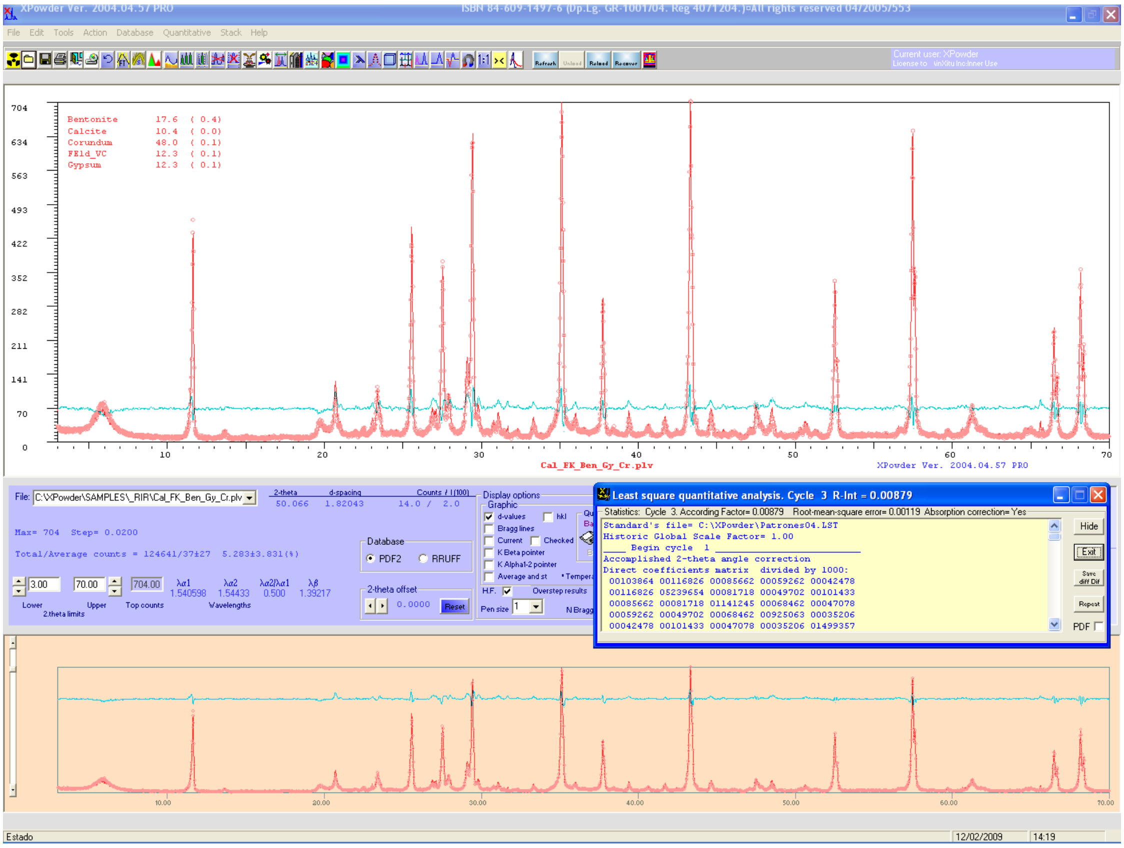


Figure 7.6.

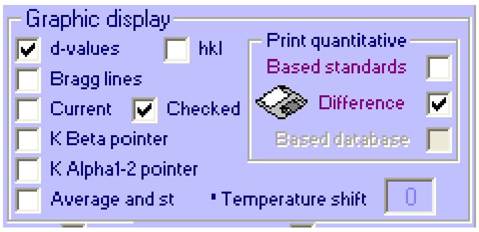


Figure 7.7.

The options on the main screen can be used (Fig. 7.7) to draw the desired details on the diffractogram graph. In the example has been marked Checked to display all the patterns selected in the tool *Matching*. It has been unchecked the box Based standards, not to be mixed on the screen the results of quantitative analysis with the names of the phases of the database. Many other alternatives are possible.

Note that we can perform a quantitative analysis regardless of one or more phases. In these cases, the difference diffractogram lie only to'experimental' stage of non-quantifiable phases.

Thus, we can save this difference file and use it later to analyze individual profiles, for example, with results generally more accurate than those obtained by deconvolution techniques. Figure 7.8 shows a quantitative adjustment as shown in Figure 7.6, which has excludes one of components (Bentonite). The diagram of differences, in blue, displays the diffractogram of the pure bentonite, which can then be studied separately (figure 7.9). Some peaks of other phases can not be completely eliminated and appear in the difference diffractogram as residual sharp reflections.

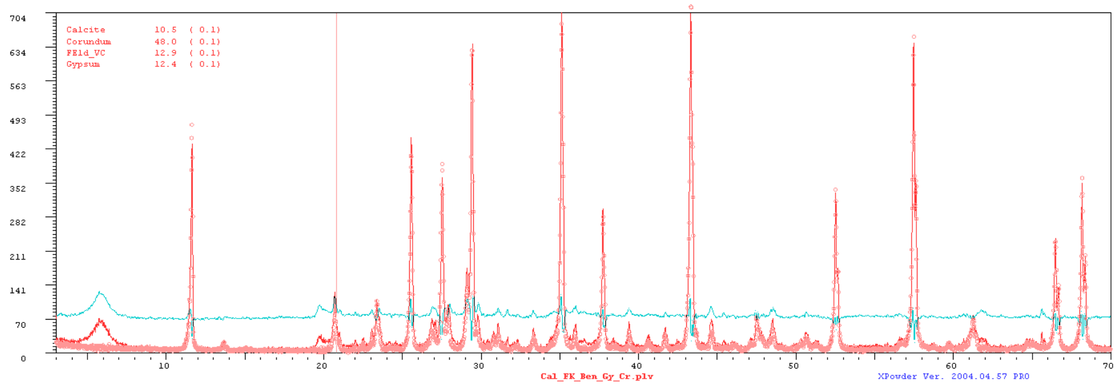


Figure 7.8.

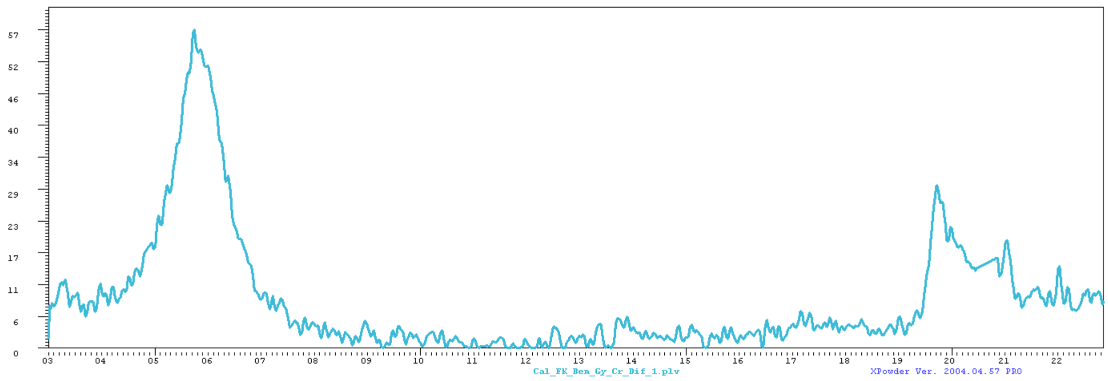


Figure 7.9. Detail of the difference diffractogram corresponding to Figure 7.8 where you can appreciate the isolated pattern of bentonite.

The partial results and other calculation details are displayed on-screen text of a yellow background (Fig. 7.6) and are recorded in the '*log file*', as shown in the following list:

```
--------------------------------------------------------------------------------
Least squares quantitative analysis Section. Sample: C:\XPowder\SAMPLES\D.plv
Full profile refinement method
Standard's file= C:\XPowder\Salts.LST
__________________________________________
Historic Global Scale Factor= 1.00
____ Begin cycle  1 __________________________
Accomplished 2-theta angle correction
Direct coefficients matrix  divided by 1000:
 00340479 00219720 00007577 00017374
 00219720 00469209 00029085 00025070
 00007577 00029085 01140231 00009856
 00017374 00025070 00009856 00303487
__________________________
Inverse coefficients matrix (x 1000000):
 0.0042  -0.0020   0.0000  -0.0001
-0.0020   0.0031  -0.0001  -0.0001
 0.0000  -0.0001   0.0009   0.0000
-0.0001  -0.0001   0.0000   0.0033
__________________________
Correlation coefficients matrix:
 1.0000  -0.5481   0.0119  -0.0212
-0.5481   1.0000  -0.0389  -0.0434
 0.0119  -0.0389   1.0000  -0.0144
-0.0212  -0.0434  -0.0144   1.0000
______________________________
Acumulated Counts for observed diffractogram  = 51166
Acumulated Counts for calculated diffractogram= 36637
________ Composition _________
Barite        52.9      ( 0.3)
Celestin      27.5      ( 0.3)
Fluorite      09.1      ( 0.1)
Gypsum        10.6      ( 0.3)
______________________________
Sum =                     100.0      ( 1.0)
Density     3.989( 0.040) g·cm-³
Linear absorption coefficient      58.465 cm-¹
______________________________
______________________________
According factor= 0.05130     Defined as Sum[[Int(o)-Int(c)]^2]/Sum[Int(o)^2]
Relative Root-mean-square error= 0.07933
The percentages have been calculated weighing the data.
The selected composition is unsuitable or incomplete
Absorption correction= Yes
____ Begin cycle  2 __________________________
Accomplished 2-theta angle correction
Direct coefficients matrix  divided by 1000:
 00340479 00196180 00008363 00015846
 00196180 00456333 00030140 00025144
 00008363 00030140 01139641 00010019
 00015846 00025144 00010019 00325783
__________________________
Inverse coefficients matrix (x 1000000):
 0.0039  -0.0017   0.0000  -0.0001
-0.0017   0.0029  -0.0001  -0.0001
 0.0000  -0.0001   0.0009   0.0000
-0.0001  -0.0001   0.0000   0.0031
__________________________
Correlation coefficients matrix:
 1.0000  -0.4962   0.0088  -0.0176
-0.4962   1.0000  -0.0398  -0.0473
 0.0088  -0.0398   1.0000  -0.0139
-0.0176  -0.0473  -0.0139   1.0000
______________________________
Acumulated Counts for observed diffractogram  = 51166
Acumulated Counts for calculated diffractogram= 37131
________ Composition _________
Barite        54.6      ( 0.7)
Celestin      25.8      ( 0.6)
Fluorite      08.7      ( 0.3)
Gypsum        10.9      ( 0.6)
______________________________
Sum =        100.0      ( 2.1)
Density     3.994( 0.084) g·cm-³
Linear absorption coefficient      59.394 cm-¹
```

```
_____________________________
_____________________________
According factor= 0.02407     Defined as Sum[[Int(o)-Int(c)]^2]/Sum[Int(o)^2]
Relative Root-mean-square error= 0.07685
The percentages have been calculated weighing the data.
Absorption correction= Yes
____ Begin cycle  3 _________________________
Accomplished 2-theta angle correction
Direct coefficients matrix  divided by 1000:
 00322047 00196784 00008635 00013832
 00196784 00469212 00029085 00026019
 00008635 00029085 01140231 00010886
 00013832 00026019 00010886 00325783
_________________________
Inverse coefficients matrix (x 1000000):
 0.0042  -0.0017   0.0000   0.0000
-0.0017   0.0029  -0.0001  -0.0002
 0.0000  -0.0001   0.0009   0.0000
 0.0000  -0.0002   0.0000   0.0031
_________________________
Correlation coefficients matrix:
 1.0000  -0.5049   0.0070  -0.0106
-0.5049   1.0000  -0.0369  -0.0515
 0.0070  -0.0369   1.0000  -0.0153
-0.0106  -0.0515  -0.0153   1.0000
_____________________________
Acumulated Counts for observed diffractogram  = 51166
Acumulated Counts for calculated diffractogram= 37711
________ Composition _________
Barite        49.4      ( 0.7)
Celestin      30.6      ( 0.6)
Fluorite      08.9      ( 0.3)
Gypsum        11.2      ( 0.6)
_____________________________
Sum =                    100.0      ( 2.2)
Density     3.963( 0.086) g·cm-³
Linear absorption coefficient      56.124 cm-¹
_____________________________
_____________________________
According factor= 0.01662     Defined as Sum[[Int(o)-Int(c)]^2]/Sum[Int(o)^2]
Relative Root-mean-square error= 0.07821
The percentages have been calculated weighing the data.
Absorption correction= Yes
____ End   cycle  3 _________________________
```

[Home]

Chapter 8. Pattern stacking. (See also 'Rearranging diffraction patterns' and 'Homogenization of 2θ scan intervals and steps' in New features of ver 2010.01.10).

XPowder can work simultaneously with a maximum of 50 diffractogram patterns. In this way, is also highlighting aspects that are not seen when working with isolated diffractograms, such as phase transitions, composition or crystallinity. The program allows the representation in perspective (3D) and by projection with level curves and, or, false color (2D).

3D Screen

To enter the 3D display (Figure 8.1) uses the button or the command 'Stack' from the main menu.

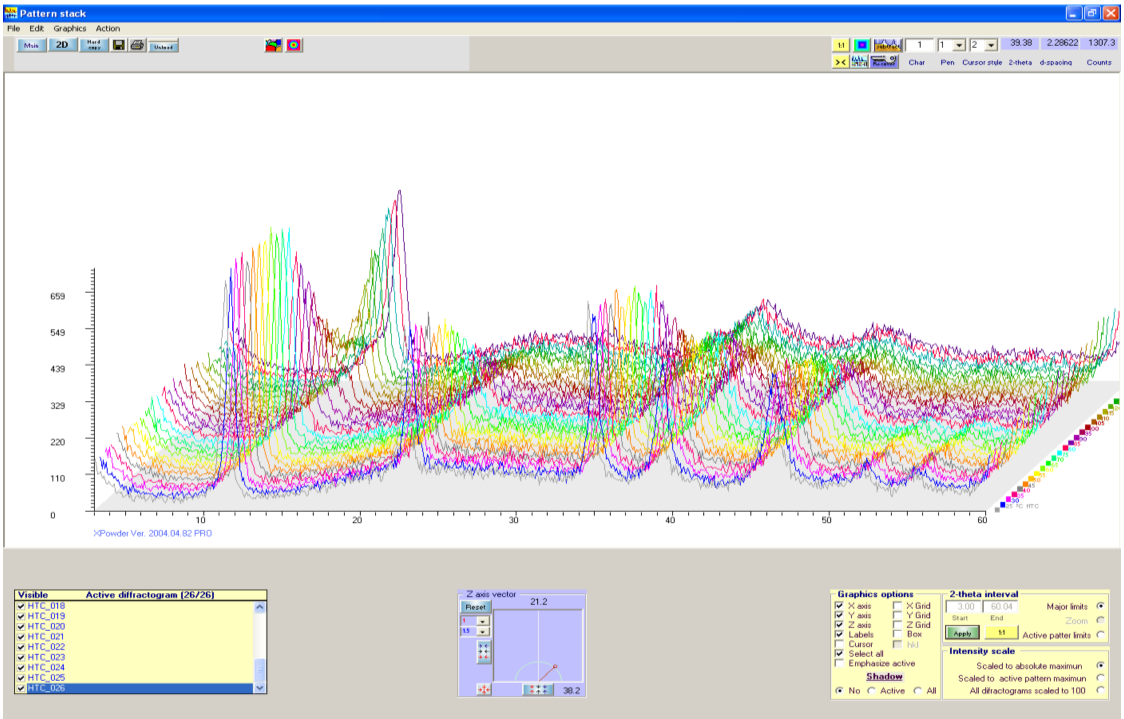


Figure 8.1. 3D Visualization of a sequence with a recorded temperature variation.

The blue bar from the list on the left shows the diagram of the main screen active and can be changed by clicking on the list with the left mouse button. Fields marked (☑) correspond to the patterns that are drawn on the figure. It can be selected manually.

The tool Z-axis vector can control the direction and depth of the third axis (Z) by dragging the red dot on the small screen of a blue background. The buttons , and set to zero displacement of the axis vertical, horizontal or both respectively. 1.5 modify the sensitivity of the drag of the mouse on this screen. 1.5 change the height of the patterns, enabling the stack as the figure of 8.4.

The tool Graphics options selects the items shown in the graphic (axes, background, labels, etc.) or highlight the active pattern (Emphasize active).

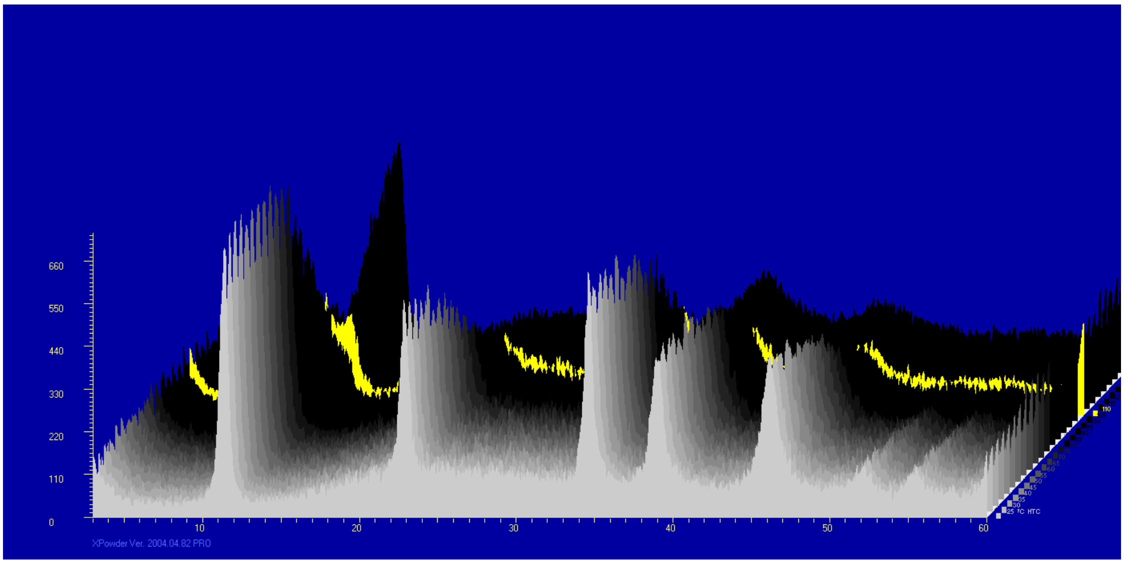
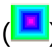


Figure 8.2

In figure 8.2, have used a gray color palette (), a blue background () and has set the active chart with a specific color ( yellow).

In Figure 8.3 has been removed to fund the entire package (Bgnd).

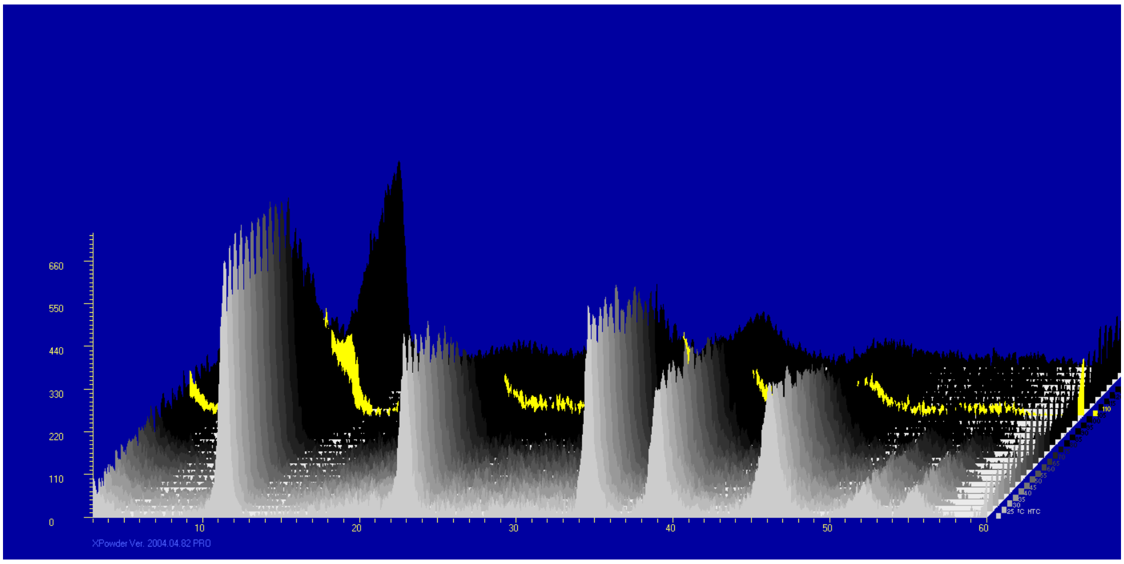


Figure 8.3.

You can use the matching tool, both in the 3D and in the 2D representations, in order to graphically superimpose database records in experimental patterns. Figure 8.4 shows an example in 3D (tick box hkl). In presenting 3D is necessary to put the horizontal scroll to zero (it can be used to the button )

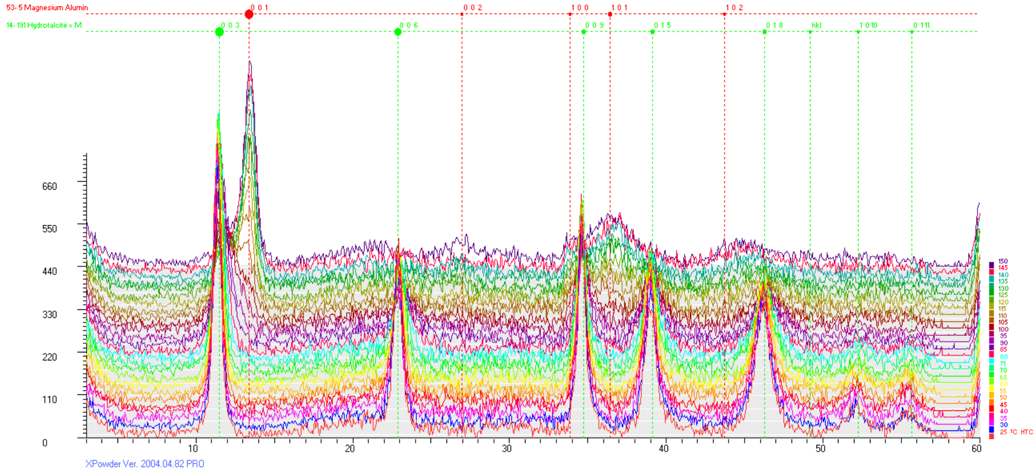


Figure 8.3.

Figure 8.4 also shows the use of the tools Z-axis vector in order to visualize a sequence of the same diffratogram patters. The area of circles (red and green in the illustration) lets recognize the peaks correspond to the relative intensities of each phase of the database.

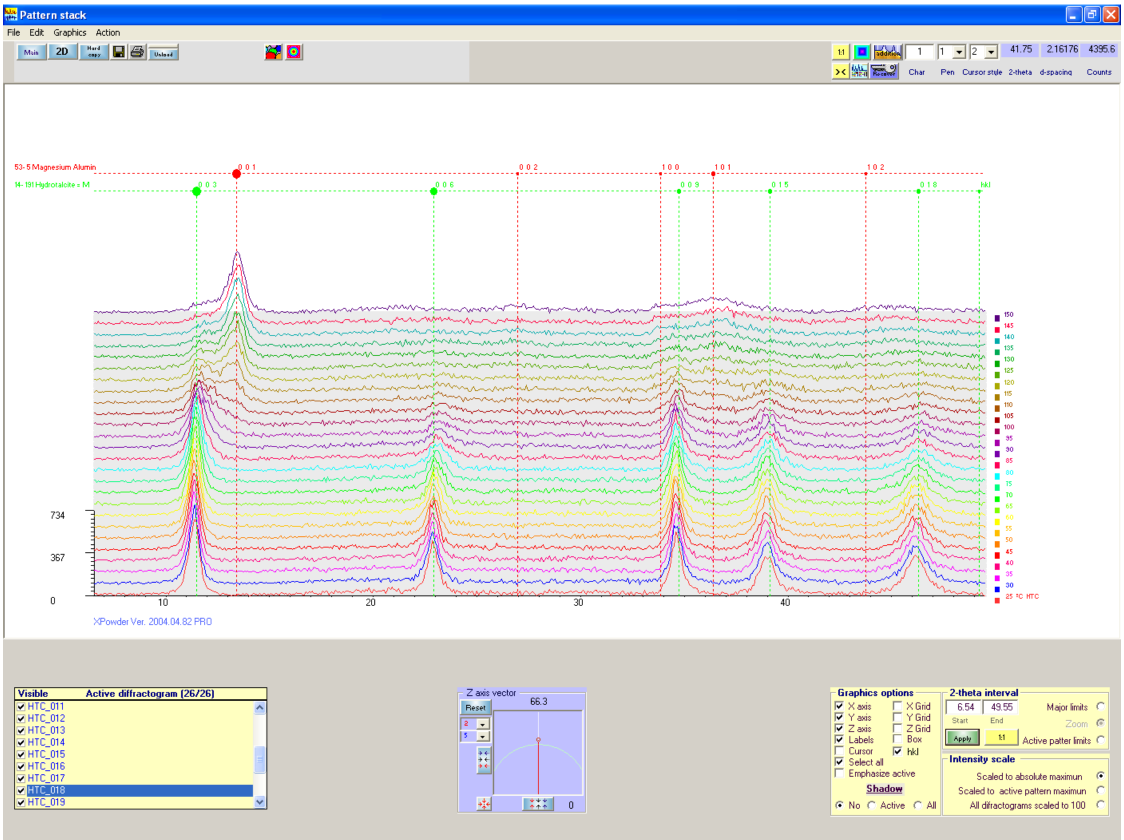


Figure 8.4.

2D Screen In this screen you can enter only from the 3D display by pressing the button 2D. The result is shown in Figure 8.5.

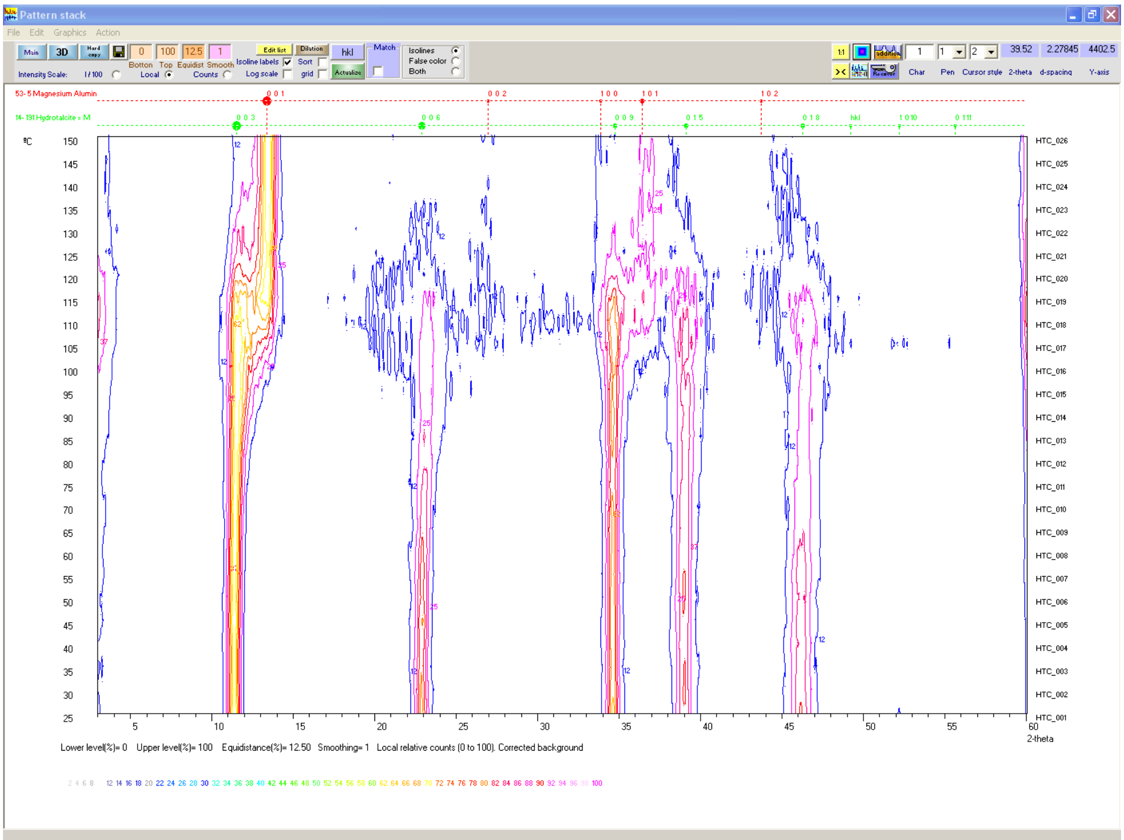


Figure 8.5

The colored curves, calculated by quadratic interpolation methods, show different scales of intensity, as the key to the bottom, and can be scaled depending on the choice (Intensity scale) to the value 100 of the respective partial patterns (Option I/I100), at maximum value of each diffractogram in the range of used 2θ (Local Option, is selected by default) or absolute (Counts). You can select a logarithmic representation (Mark Log scale)). Instead of isolines can be used false color or both representations (Isolines , False color or Both Options). You can also subtract/add background with the button Bgnd.

2θ specific intervals can be selected by clicking and dragging with the left mouse button. 1:1 and >< buttons are used to extend the 2θ interval.

Orders Edit list / Hide list allowed to edit/hide the list of patterns used for the mapping, whose file names are displayed in the right column of the chart.

The bar pattern of databases can be drawn, in combination with the tool 'Matching'. In this sense, the button hkl allows the drawing/delete these same bars directly on the map of intensities. The name of the crystalline phase and the *hkl* reflections index appear, when the cursor stops on and maximum of the intensity map (Fig. 8.6).

0 100 12.5 1 Botton Top Equidist Smooth The values of minimum isoline, equidistance, maximum isoline and surface smoothing (a value 0, produces no smoothing of the data) can be respectively introduced in these boxes.

The button  is used to redraw the map when a parameter or the list of diffractograms change.

When a data PLV format type is used, including the parameter 'Temperature', the column on the left shows a temperature values (Figures 8.5 and 8.6). If a recording of patterns has been done while the sample is heated and subsequently cooling has been recorded, it should tick Sort, to display the records in a historical arrangement and not temperature arrangement because, in the latter case, the records obtained at the same temperature, during the ascent and descent, they would appear together.

If the process is independent of temperature, the sequence of presentation list is the same used to load the respective data files.

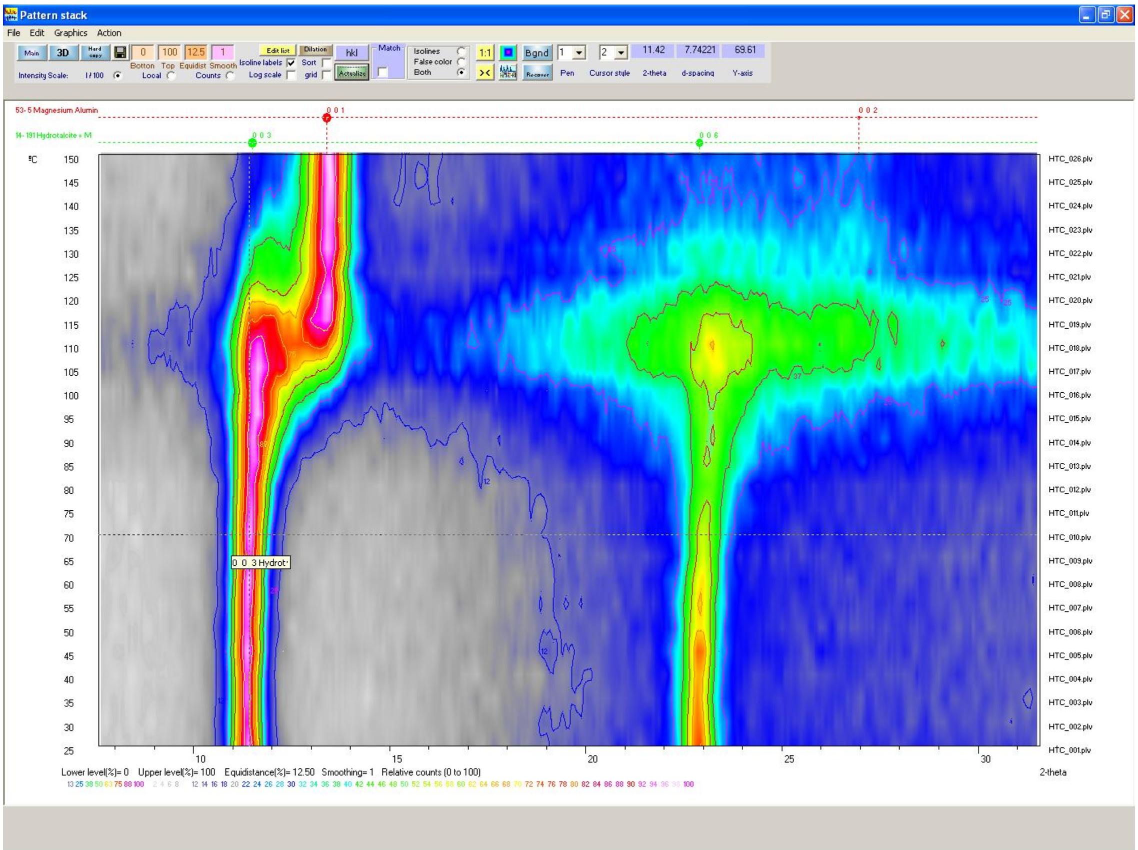


Figure 8.6. Change pf phase around the 110 º C. A widespread loss of crystallinity is observed. This is marked by the widening of the maximum that precede the formation of the higher temperature phase.

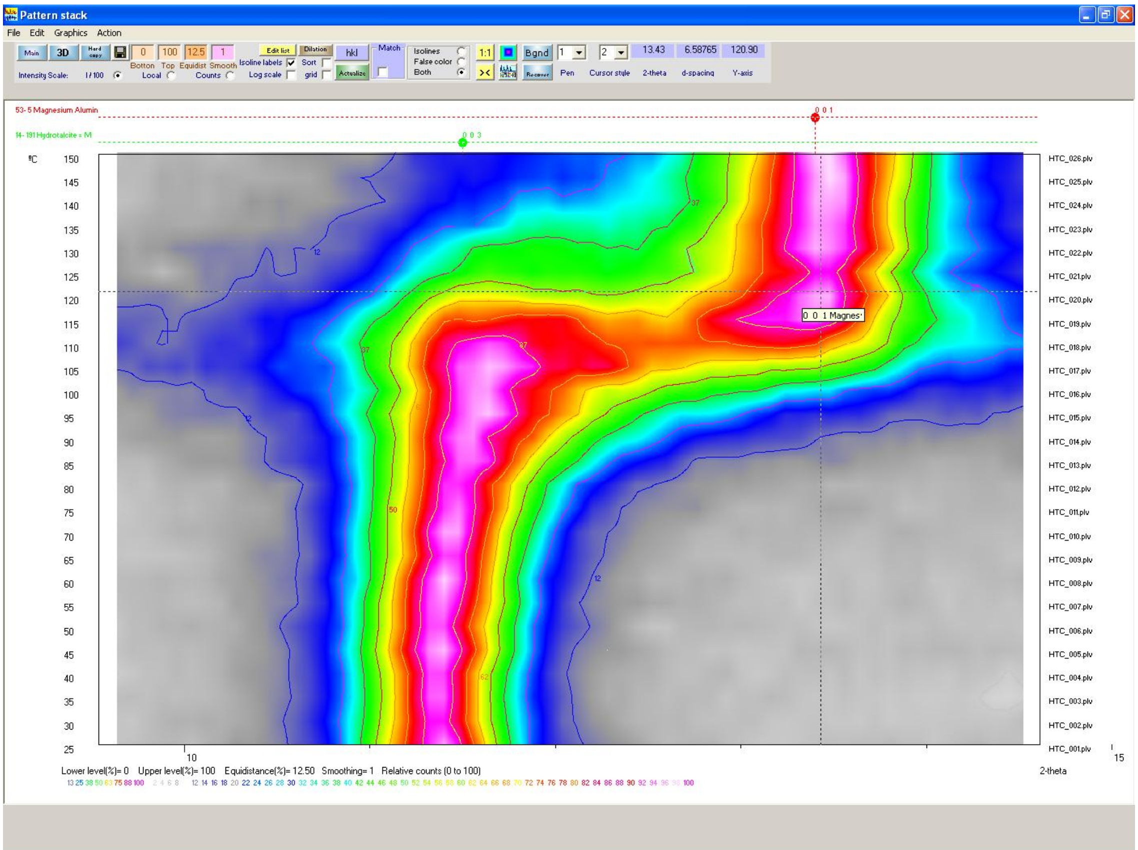
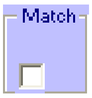
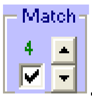


Figure 8.7. Details of the previous figure. The indexes (001) of the phase formed at higher temperatures are shown overprinted. The curve level of 50% (between yellow and green) marks the evolution of FWHM along the sequence.

Can be noted that while the 3D presentation allows patterns with any data format (RAW, UDF, TXT, etc.), with different exploration ranges of (2θ angles initial and final) and even different 2θ steps between successive intensity measures, the **2D option requires all diffractogram patterns have been registered under the same experimental conditions**, because XPowder uses nonlinear interpolation techniques for the drawing of the isolines and the calculation of the false color requiring that restriction.

By clicking on 

Is obtained 

. This eliminates the interpolation of data, which involves creating maps of the previous figures and limited representation to the original patterns (very similar to colored Debye-Scherrer patterns, Figure 8.8). The number (4 in the example of the Match) is the width of each diffractogram.

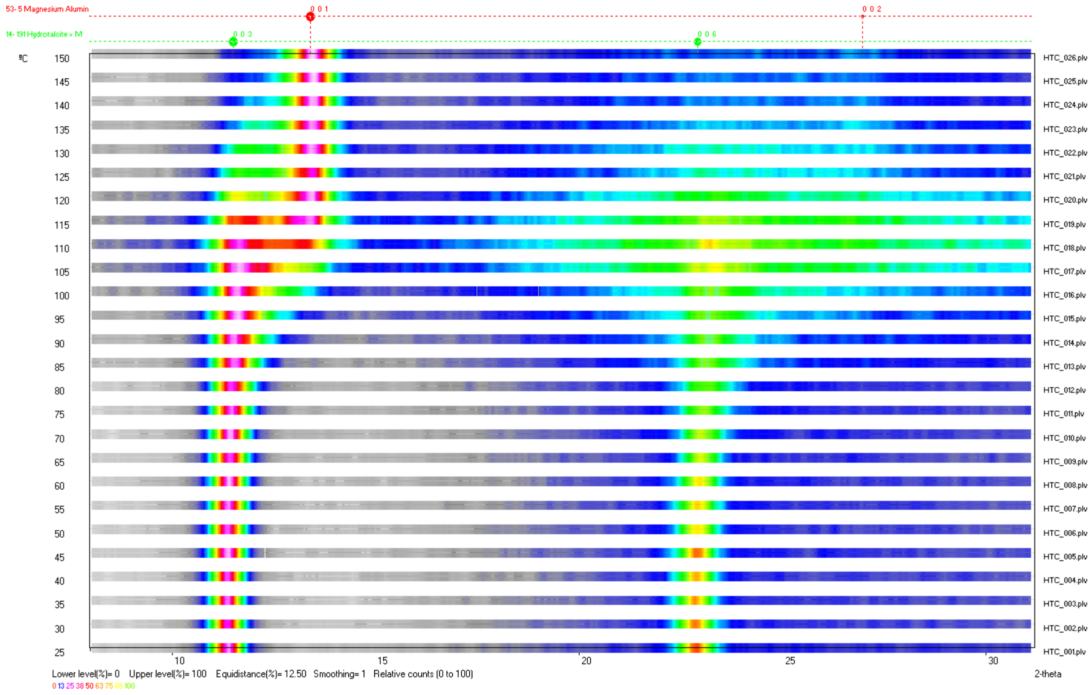


Figure 8.8.

The button  allows to do calculations of expansion coefficients. When the tool Thermal coefficients is present, simply click (while press down the Alt key) points of the map from which you want to measure the thermal dilation coefficientf. Note that you can make a measurement for each *HK*L direction, which allows studying the thermal dilation tensor (Fig. 8.9).

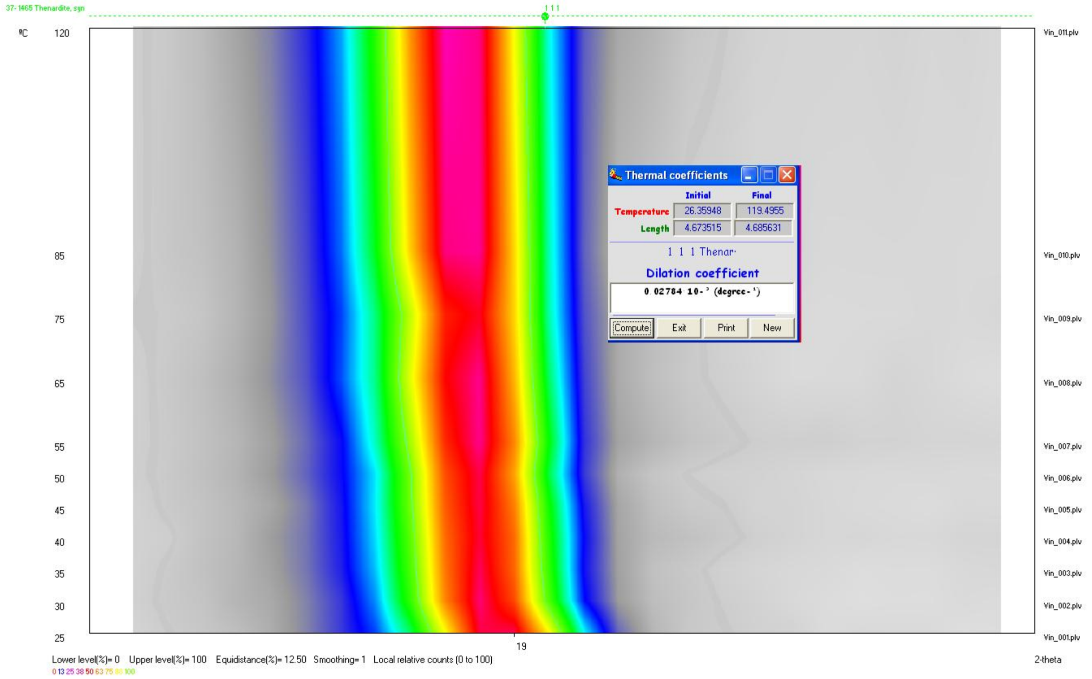


Figure 8.9.

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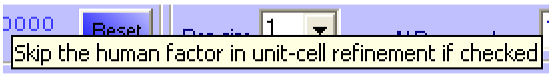
Chapter 9. Unit-cell refinement.

XPowder has an advanced tool that allows comfortably the refinement of the unit-cell even if the sample has several components. The initial parameters are approximate values a,b,c,α,β and γ. The results include the optimized new lattice parameters with corresponding statistics and the possibility to systematic study of extinctions of space-group and come to the study of the existence of partial or total superstructures.

As is well known, these data from initial cell unit are very difficult to calculate from the powder patterns, so that, wherever possible, it should be results obtained by methods of single crystal, such as those that often of database records. If the substance has been previously identified and the lattice parameters are included among the information in the database, such values can be used as initial values. When the tools' *Matching* 'is present, XPowder read them directly. It can also use the data ofcell isomorphic substances, even though the chemical composition is very different. In other cases, it is sometimes possible to calculate 'ab initio' of the unit-cell from powder patterns, through the use of specific programs, which often use methods of "trial and error ' to propose possible solutions (' TREOR ', etc).

If the box H.F. ☑ (*Human Factor*) from the initial screen is checked, most of the refining process is done automatically without user intervention, although this need not lead to better solutions.



XPowder uses a non linear least squares routine that allows the simultaneous refinement of the lattice parameters **a, b, c**, α, β and γ, and the instrumentals (horizontal and vertical) displacement of the sample.

As a general rule, it is always preferable to devote some time to make the necessary alignments in the diffractometer, rather than trusting the quality of results to the purely mathematical refinement of instrumental parameters. This is because the number of parameters to refine (6 from unit-cell and 2 instrumentals) may be too high compared to the available number of reflections. On the other hand, if the patterns are poor quality, it is possible that during the successive refinement cycles, the parameters really interesting, ranging from too bad correct values and there is no convergence in the overall refinement process.

Some parameters to refine, can be linked or fixed, so as to facilitate the calculation by using smaller matrices. For example, if the a tetragonal unit-cell is refinded, the parameters a and b can be linked(a = b) and the values of α, β and γ can be fixed **$(\alpha = \beta = \gamma = 90\equiv)$**. If, moreover, the diffractometer is correctly aligned, you can skip the instrumental correction, so that only the cell parameters a and b are refined.

Other times, particularly when there are isomorphism or order-disorder phenomena, it may be interesting to refine a unit-cell of high symmetry in a system of lower symmetry (for example, a crystal with initial orthorhombic cell can refined in monoclinic system or even in the triclinic system). This strategy is often used in structures type *spinel, perowskita, garnet,* etc.

Before making the refinement of a unit-cell, the displacement of 2θ angle should correct using a standard pattern (better internal standard), remove the component Kα_2 (*'Kα_2 stripping'*) and 'read' the d-spacings of experimental pattern (better manually through the left mouse button on the main chart which automatically). The elimination of the component Kα is not indispensable, but in many cases can improve the precision of refined parameters up an order of magnitude. It is not desirable to do background subtraction in any case.

The process of refinement can be accessed from various parts of the program. For example, in the initial screen, the button ☐ comes directly to the refinement tool (Figure 9.3). However, it is always desirable that the tool '*Matching*' is present, and that the initial crystalline phase is the current one. Simply press the button Unit-cell of this tool to obtain the refined unit-cell or to do further refinement cycles.

In the example in Figure 9.1, the program is available to refine the unit-cell of the mineral 'Celestine', having been identified and incorporated into the tool '*Matching*'. It is observed that the HF check-box of the main screen is selected. The phase, which provides the initial lattice

parameters is the third of the tool '*Matching*', which appears in the figure on a blue band (Celestine).

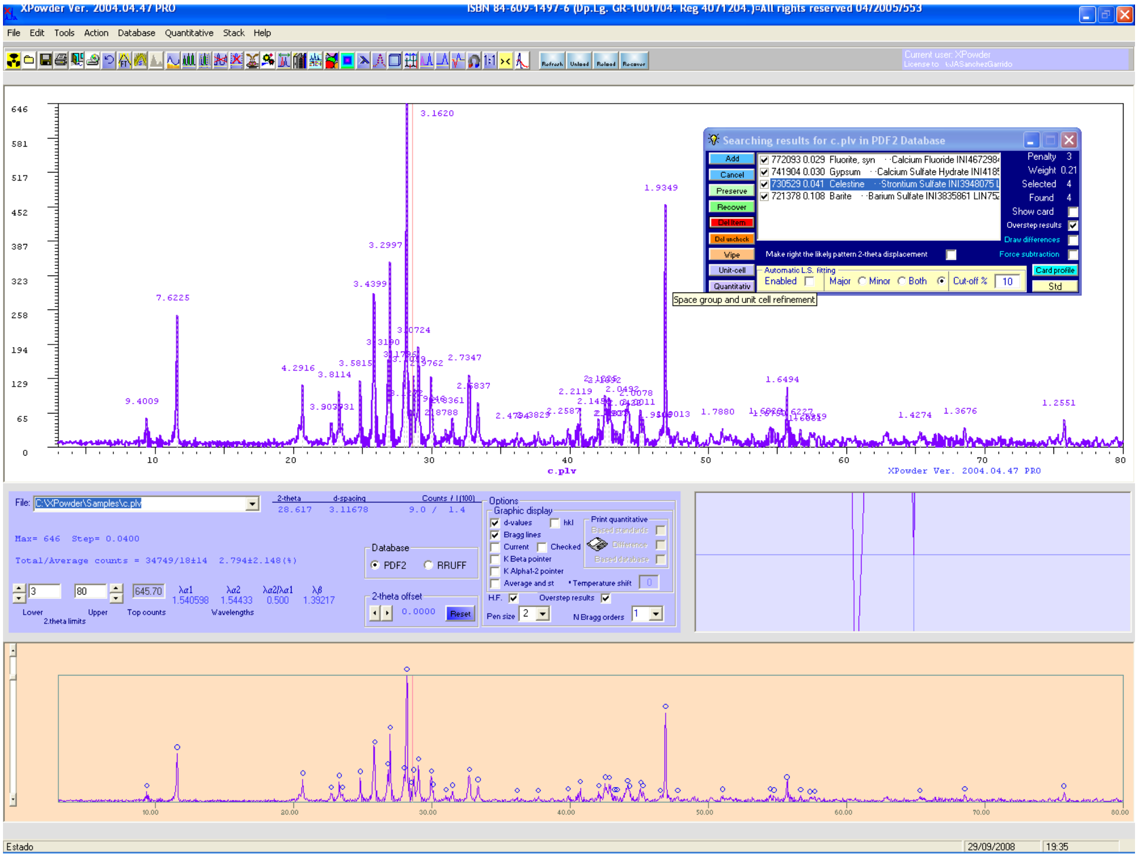


Figure 9.1.

By clicking Unit-cell comes the unit-cell refinement process. In Figures 92 and 93, shows that the program has performed automatically constraints due to the space group of crystalline phase (orthorhombic P lattice, $\alpha = \beta = \gamma = 90$) and restraints for the instrumental alignment parameters. The values of the initial and refined unit-cell, including statistical and volume are also shown directly.

It can see that in the main graphic (figure 9.2) have been drawn calculated HKL lines for the refined unit-cell, but in a primitive and lacking space symmetry elements (screw axes or glide planes). HKL types are grouped by colors at different heights. The colors correspond to those of the axes of the Unit cell parameters framework. The reflections h00, 0k0, 00l, 0kl, h0l, hk0 and hkl show from top to bottom. This distribution is done to facilitate the fast identification of isolated reflections. These can be studied in detail by 'zoom' on the upper main graphic (Shift + left mouse button), or in the lower secondary display.

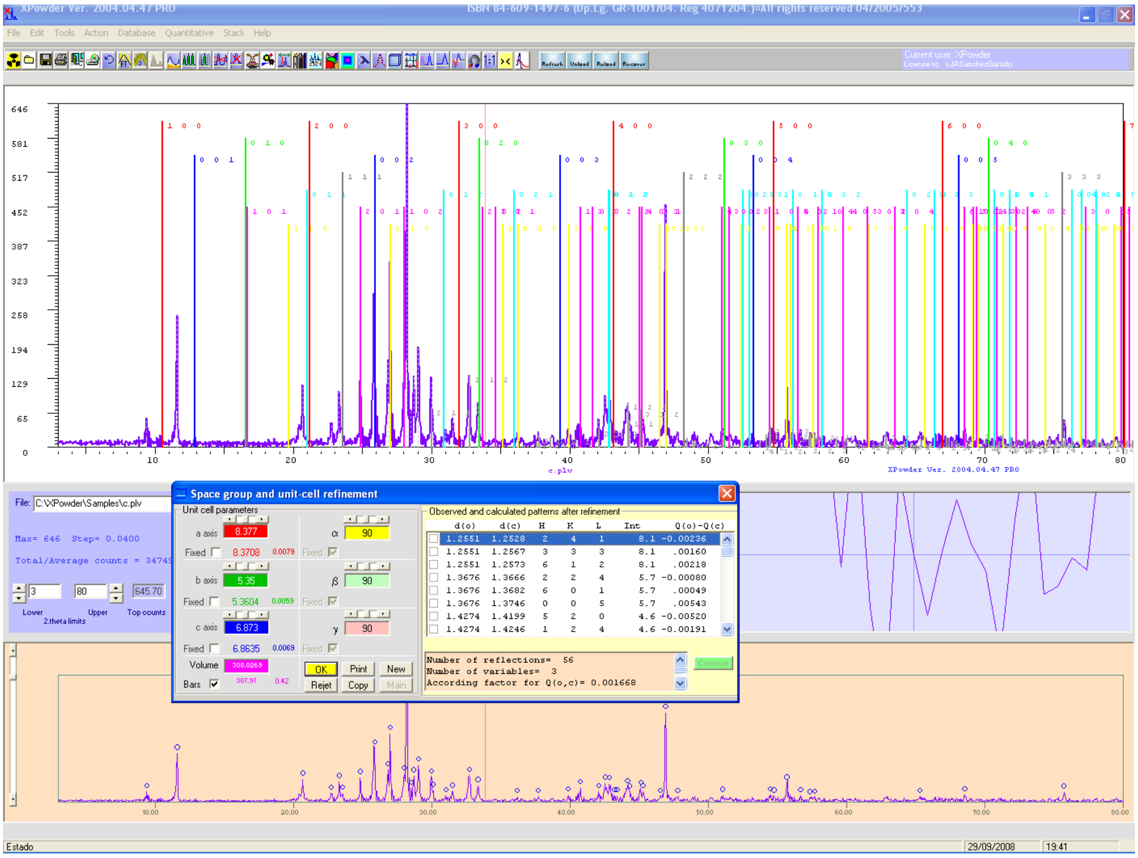


Figure 9.2

By pressing OK will get the figure 9.3.

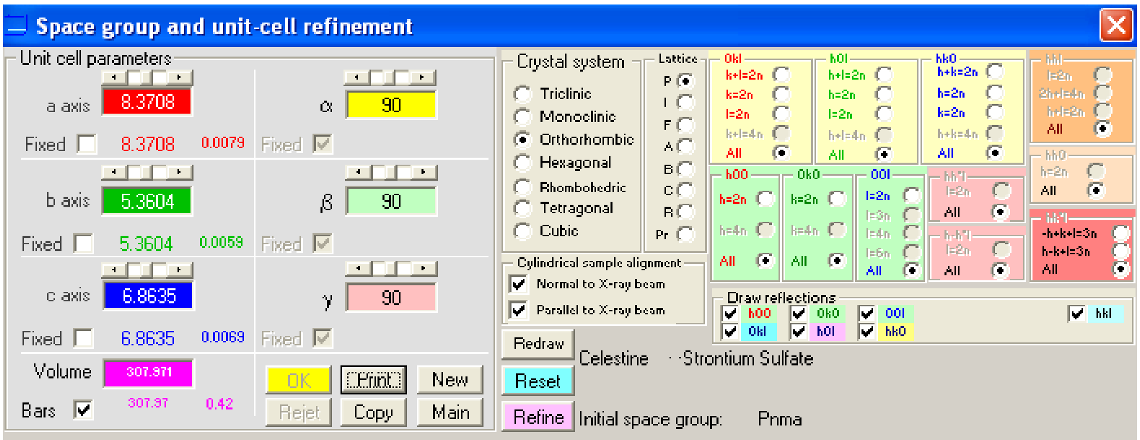


Figure 9.3.

From the screen shown in Figure 9.3 is you can do:

- Show / Hide bar chart of the refined unit-cell. (Box Bars).
- Restrict the drawing of hkl reflection groups attached to specific symmetry space elements (Bravais lattices, screw axes or glide planes, '0kl, h0l,..., hh*l' framework) . Initially there are no restrictions except those due to the lattice type. It can see that by stopping the cursor on the respective option buttons, a message appears overlapped, which contains information on the space symmetry associated with the systematic extinctions, linked to each HKL group, which facilitates the study of space group.
- Redraw reflections (Redraw).
- Draw the reflections by groups (Framework Draw reflections).

- Modify 'manually' values calculated using cell cursors for each crystallographic parameter.
- Fix/Refine parameters in the next cycle (Fixed check-box of each crystalline parameter or instrumental parameters of the framework Cylindrical sample alignement.
- Changing the crystalline system and Bravais lattice for the next cycle of refinement.
- Ignore the results in order to initiate a new unit-cell refinement with different conditions (Reset).
- Print graphic (Print).
- Copy the graphic to the clipboard (Copy).
- Back to the main menu (Main).
- Make the refinement of another crystalline phase of the specimen pattern and listed in the tool '*Matching*' (New).
- Perform a new cycle of refinement using the refined parameters such as new initial parameters (Refine).

Refine eliminates the HF selection (human factor), so all the following calculations will be controlled by the operator. The tool appears now as in Figure 9.4.

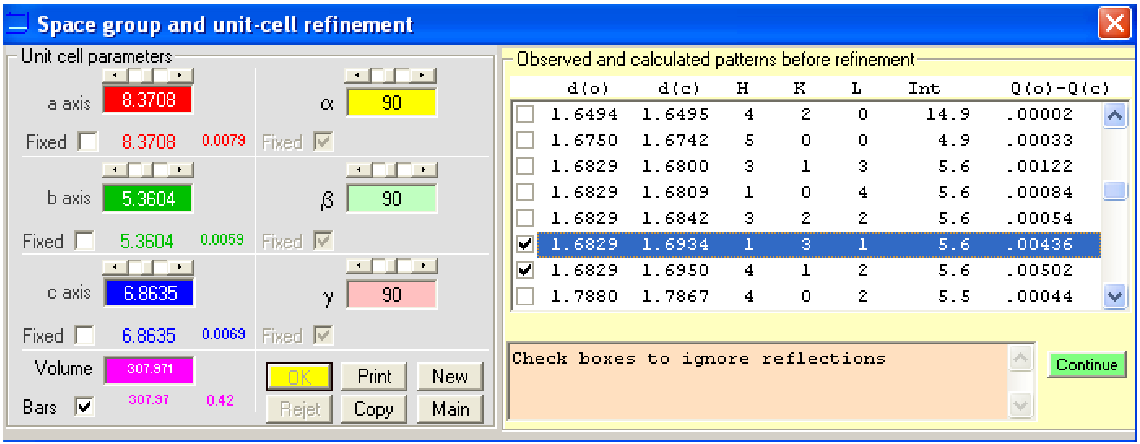


Figure 9.4.

La lista de la derecha muestra los valores de espaciados observados d(o) y calculados d(c), índices *hkl* de cada reflexión, *intensidades observadas* referidas a cien y la diferencia entre los cuadrados de los vectores recíprocos observados y calculados Q(o)-Q(c). Se puede recorrer la lista y eliminar del cálculo (marcar ☑) aquellas reflexiones cuyo valor 'Q(o)-Q(c)' sea excesivo ($Q_{hkl} = 1/d^2_{hkl}$). En el ejemplo de la Figure 9.4 se indica al programa que debe prescindir de las reflexiones *131* y *412* , ya que están marcadas. En este punto el programa queda detenido hasta que se pulsa la tecla Continue , lo que proporcionará nuevos resultados (Figure 9.5) muy semejantes a los de la Figure 9.4, ya que apenas se han modificado las condiciones del afinamiento.

The list on the right of Fig 9.4, shows the observed d(o)and calculated d(c) d-spacings, HKL reflection index, observed intensities referring to 1000 (Int) and the difference between the observed and calculated squares of reciprocal vectors Q(o)-Q(c). The list can be scrolled to eliminate of the refinement (tick ☑) those reflections whose value 'Q (o)-Q (c)' is excessive ($Qhkl = 1/d^2_{hkl}$). In the example in Figure 9.4, we have decided that the program rescinds the 131 and 412 reflections (which were already marked for this purpose). At this point, the program is paused until you press the button Continue , which will provide new results (Fig. 9.5) very similar to the figure of 9.4, just because we have slightly modified the terms of refinement.

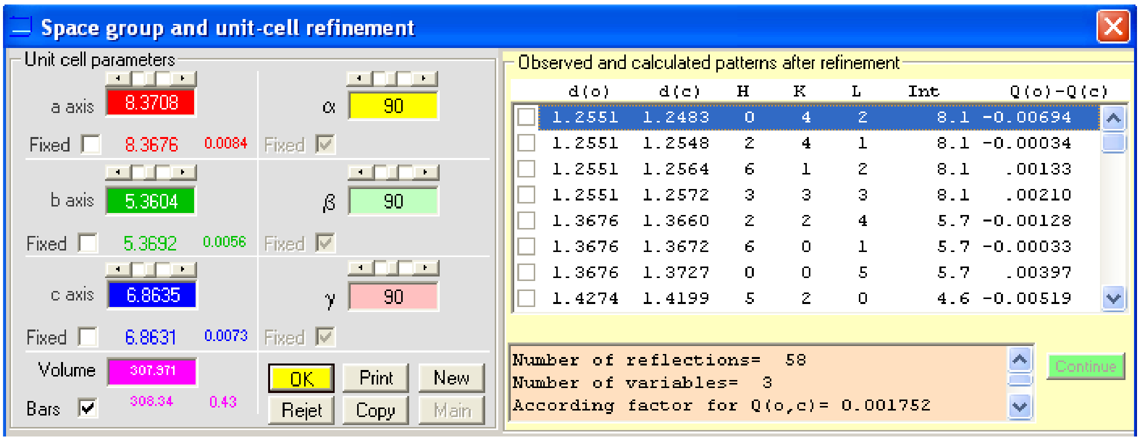


Figure 9. 5.

Under the list of figure 9.5 there is a summary which contains the number of data used in the latest refinement (58), the number of refined variables (lattice axes **a**, **b** and **c**), and the overall According factor for Q (or, c) that, being very close to zero, indicates that the refinement has been done correctly. In addition to this, the calculated errors for each of the results are obvious signs of quality refinement (0.0084 Angstroms for a-axis, 0.0056 for b-axis, 0.0073 for c-axis and 0.43 cubic Angstroms for unit-cell volume).

With the New order (Fig. 9.5), the unit-cell refinement of another component of the sample can be done. In the example, by choosing 'Gypsum' and clicking Unit cell , the results for the new phase are obtained directly (Fig. 9.6).

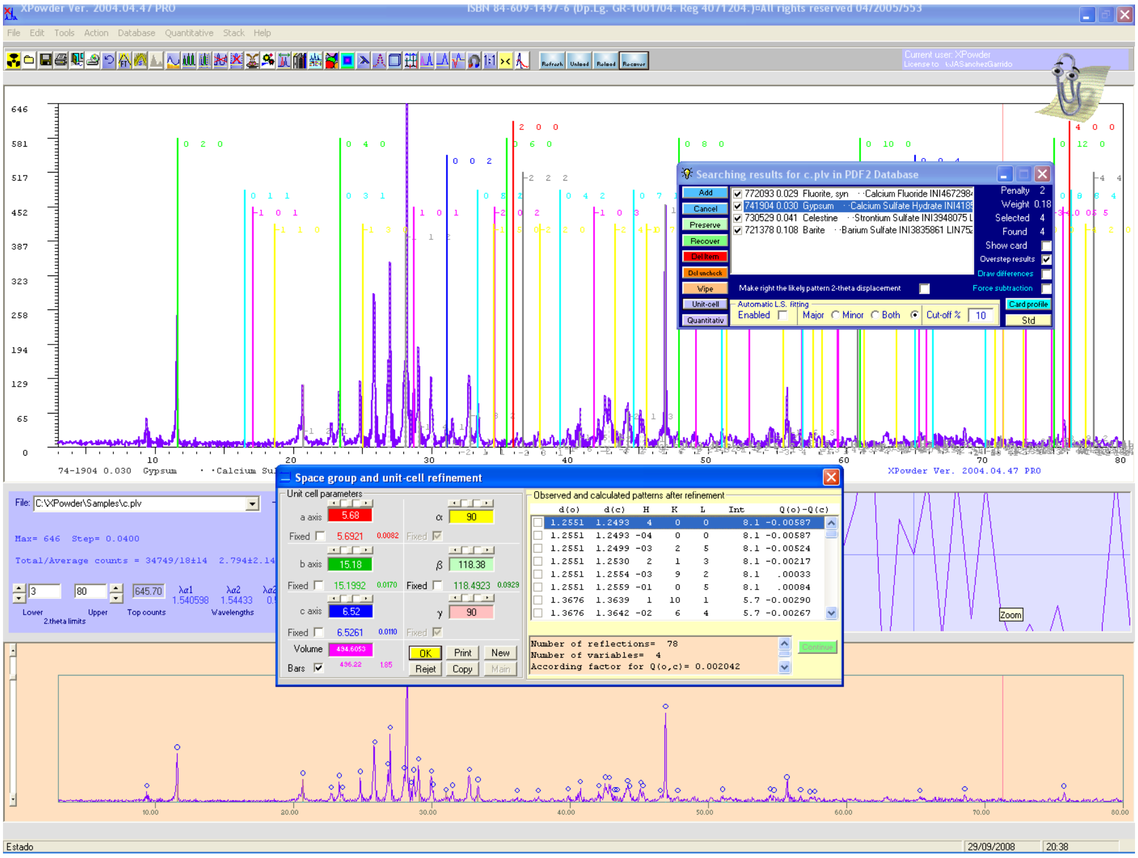
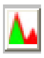
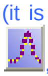


Figure 9.5. To summarize, in order to refine the unit-cell of each phase, the cursor is placed on it in the tool '*Matching*' and the button Unit-cell is then pressed. The procedure can be repeated for each identified phase. See details in the text.

Example: The determination of the ratio Ca / Mg in magnesium carbonates by PXRD is usually performed through unit-cell refinement. The most likely result is obtained then by linear interpolation between the parameters of cell in terms of extremes which have well established unit-cell parameters and chemical composition. This is the general procedure used to obtain the exact term of any mineral having solid solution composition. What makes XPowder interesting for this analysis is that this program calculates unit-cell parameters with a single mouse click.

Example: By using the program XPowder, this **real** example has been developed in approximately two minutes. Adjustment charts come from previous experiences.

1. Load a *Calcite* diffraction pattern.

2. $K_{\alpha 2}$ stripping  (it is an optional but advisable action). On the other hand, the internal standard and the 'spline' interpolation function , can improve the quality of the unit cell refinement.

3. Searching (i.e., 'one click searching'  or 'advanced searching' )

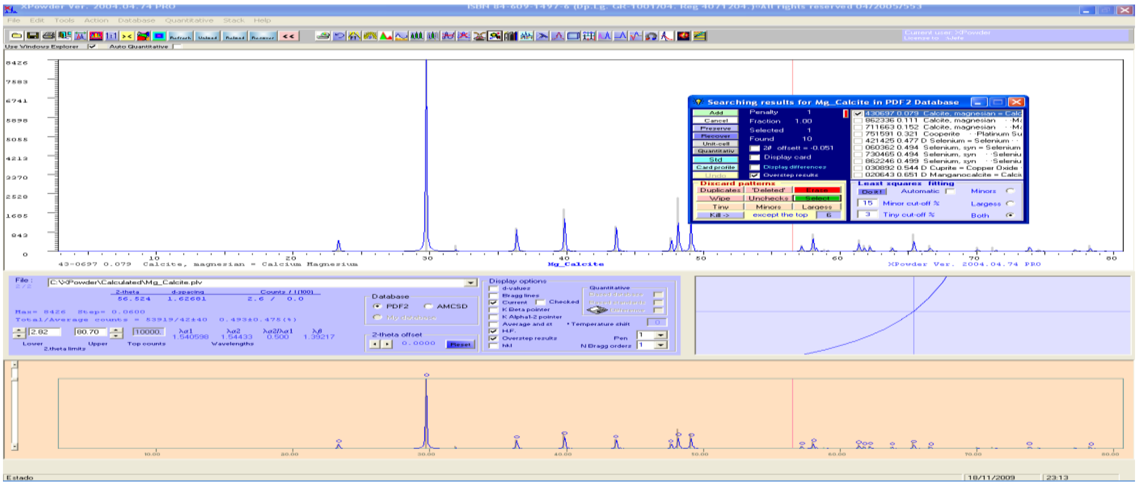


Fig 9.6

4. Click Unit-cell refinement (Unit-cell)

5. Click OK . The unit cell is now refined:

a-axis = 4.9361 ± 0.0040 Å ***c-axis*** = 16.8475 ± 0.0219 Å

Unit cell volume = 355.49 ± 0.59 Å^3

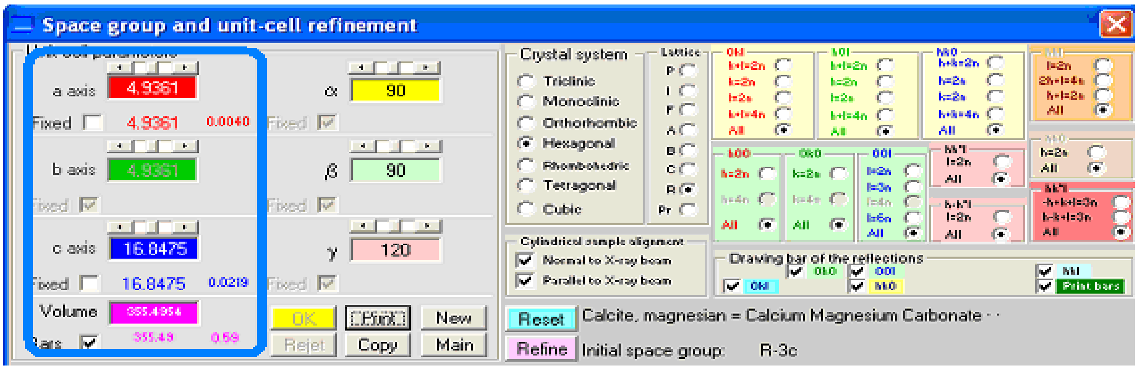
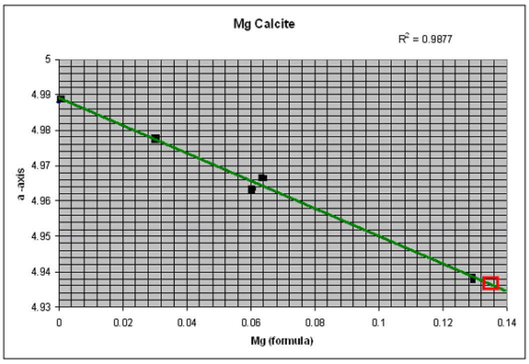


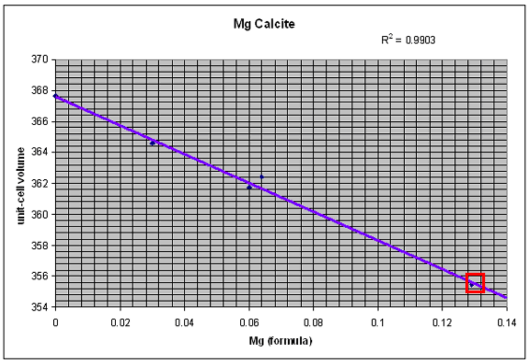
Fig 9.7

6. Error assessment: **Δ[Mg] = *m* · Δ(p)** ; where · **Δ(p)** = error of the crystallographic parameters or unit-cell volume and ***m*** slope of the adjustment line.

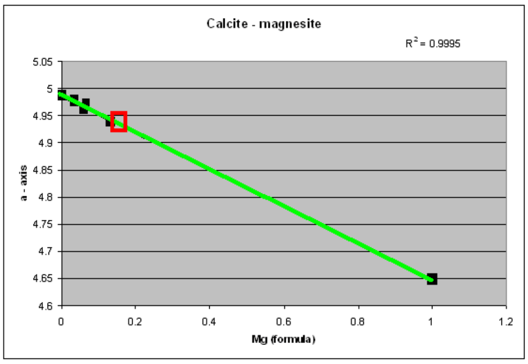
7. Results: The magnesium content of the specimen can be calculated using varied linear regression lines (Fig 1 to 6).



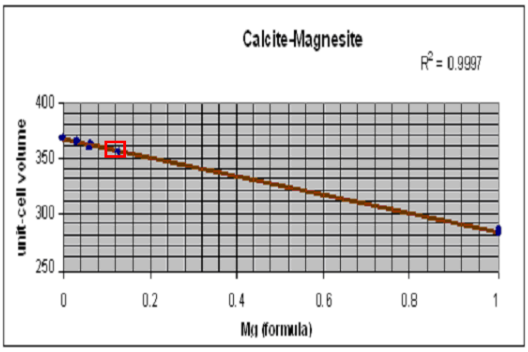
<u>Fig 9.8</u> **$Mg_{(formula)}$** = -2.5548· **a** + 12.79533= 0.13 ± 0.01



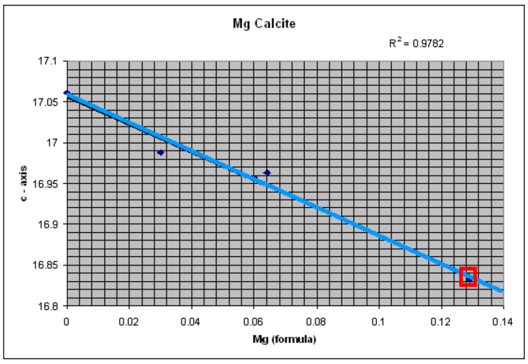
<u>Fig 9.12</u> **$Mg_{(formula)}$** = -0.0119· **Volume** +4.35=0.13±0.04



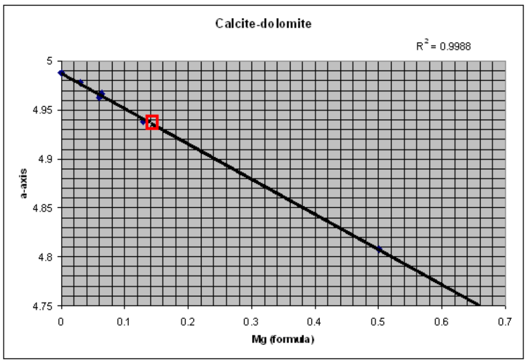
<u>Fig 9.9</u>. **$Mg_{(formula)}$** = -2.935· **a** + 14.62516= 0.13 ± 0.01



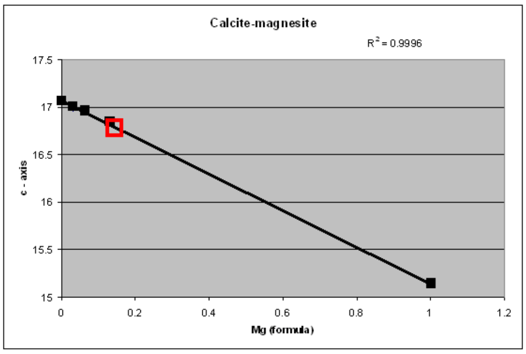
<u>Fig 9.13</u> **$Mg_{(formula)}$** =-0.0107 ·**Volume**+3.94 =0.12 ±0.04



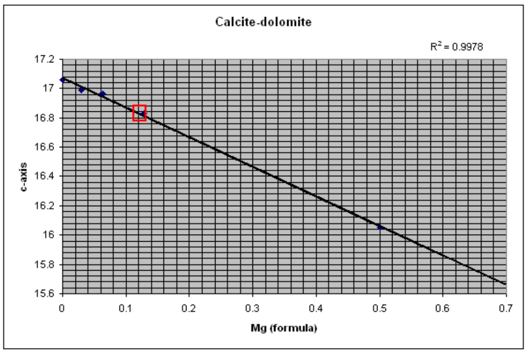
<u>Fig 9.10</u> **$Mg_{(formula)}$** = -0.587·**c** + 10.00645 = 0.12 ± 0.01



<u>Fig 9.14</u>. **$Mg_{(formula)}$** = -2.77932 ·**a** +1 3.86 = 0.14 ± 0.01



<u>Fig 9.11</u> **$Mg_{(formula)}$** = -0.5188· **c** + 8.855 = 0.12 ± 0.01



<u>Fig 9.15</u> **$Mg_{(formula)}$** = -0.494169 ·**c** + 8.437 = 0.11 ± 0.01

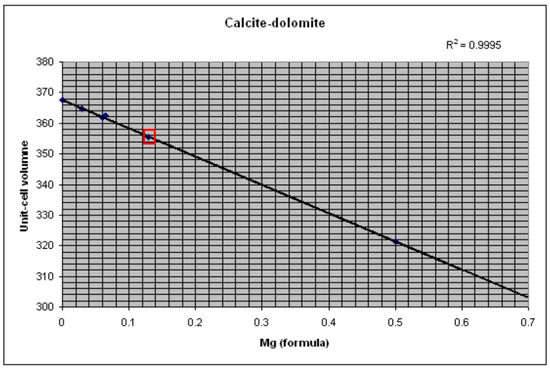


Fig 9.16. Mg$_{(formula)}$ = -0.01083 ·**volume** + 3.98 = 0.13 ± 0.04

Black points: Regression data from experimental chemical and PXRD analysis. Data of the 'Mg content = 0.5' point in the figs. 7 , 8 and 9 are of pure dolomite. Data of the 'Mg content=1' point in the figs. 2 , 4 and 6 are of pure magnesite. Data of the 'Mg content=0 are of pure calcite. **Unit-cell volume = a · a · sin(120) · c** (figs. 5 and 6).

Red squares: PXRD data from example

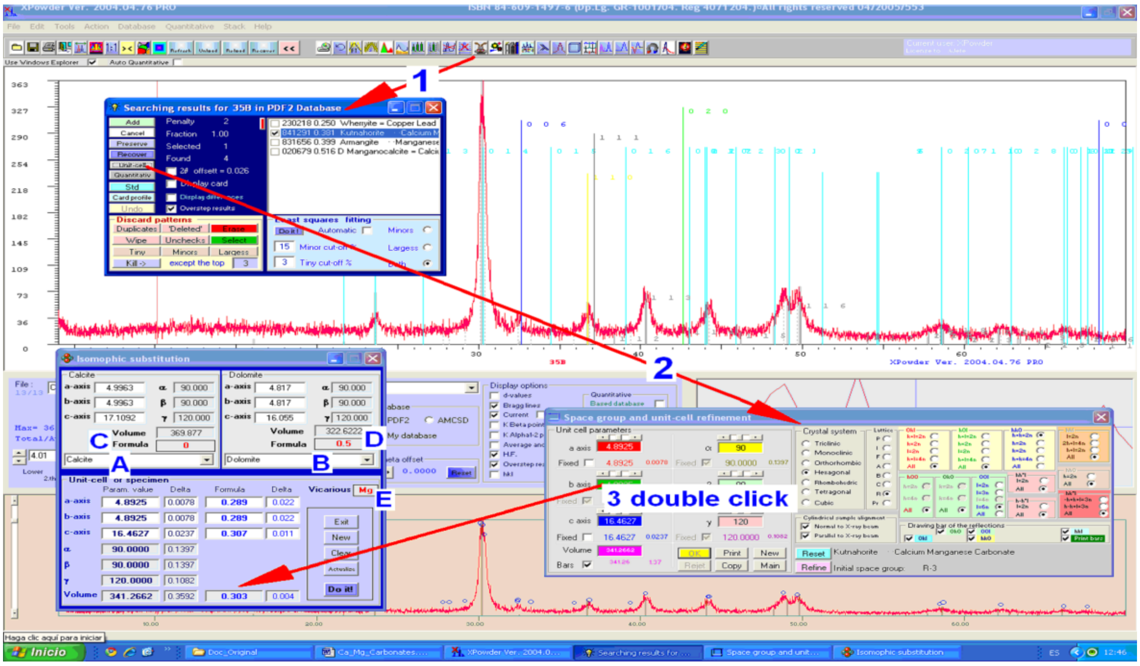


Fig 9.17 XPowder Program can do this automatically using a tool that calculates the terms interpolated from the values of ending cells. This tool is derived from the main menu (**tools ► Solid Solution**), or from the **cell refinement** tool, by double clicking on the text box of any lattice parameter. In the example, a carbonate type *'Mg-Ca kutnohorite'* has been identified (1) . The unit cell is refined (2) . Then, the exact term of the series is obtained by double clicking on the box of the refined parameter ***b*** (3). The extreme terms and vicariant elements can be changed into A, B, C and D. The editable file '*SolSol.txt*' in the program directory, is a collection of unit-cell of exact composition phases as in the example:

Calcite
4.9963
4.9963
17.1092
90
90
120
Dolomite
4.808
4.808
16.055
90
90
120
Magnesite
4.646
4.646
15.139
90
90
120

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Chapter 10. Profile Analysis.

The reflection profiles provide information on the crystallinity. This concept can not be defined uniquely as it covers many aspects of the real crystal, as are the average crystal size, the size and distribution of crystal mosaic (it is often called in diffraction as 'coherent domain'), its form and habit, uniformity in both, dimensions (including here the inhomogeneous deformation due to active or residual tension) and composition of the lattice, etc.

This leads to significant changes to four elements of the observable profile:

- Absolute and relative values of the integrated intensity of the profile.
- Profile broadening.
- Distribution function.
- Asymmetry.

Absolute and relative values of the integrated intensity. Increases with the square of the average radio of the crystal sections, perpendicular to each reciprocal vector, which produces the HKL reflection. In the same way, the average of absolute intensity of the total diffracted by a powder sample is a good measure of its overall crystallinity. By contrast, the 'relative average' value, the most general expressed as a percentage (and also its standard deviation), is inverse function of the overall crystallinity (the latter two figures are virtually independent of the experimental conditions). All this are applied both to individual reflections and full pattern. Here, the concept of crystallinity refers primarily to the size of grain. These values are displayed directly by the program when the sample is loaded. These figures appear on the screen in numerical or graphic forms when the Average and st has been checked (Figure 10.1).

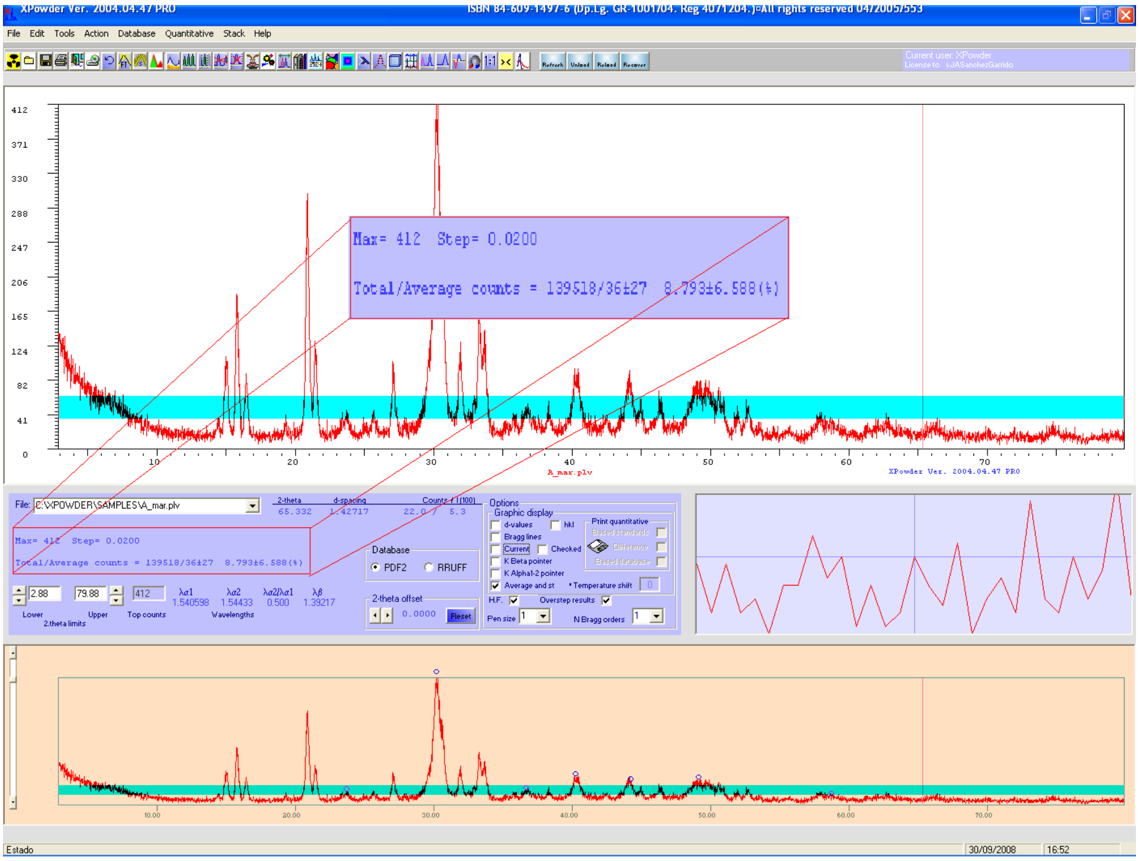

Figure 10.1. The base of the blue-green band is the average for the overall intensity of the pattern. The height of the band is the standard deviation. The crystals are small (Struvite). The average value of intensities is% 8793 ± 6588

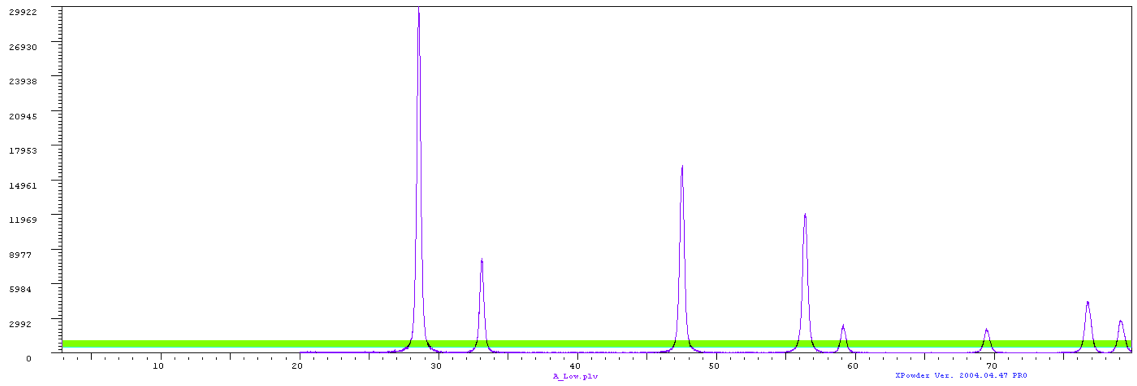

Figure 10.2. The pattern corresponds to a mid-sized crystasl specimen (CeO). Average intensities (%) = 0848 ± 1703

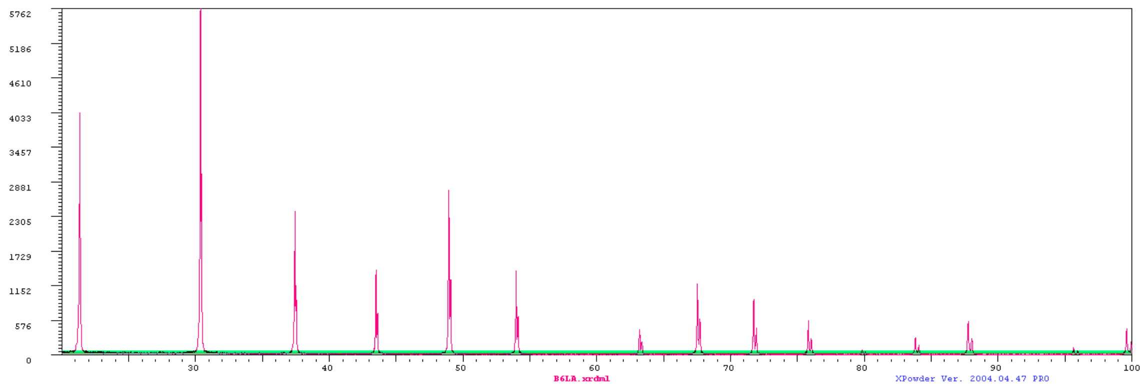

Figure 10.3. Pattern of large crystals specimen **(B_6La)**. Average value of intensities (%) = 0.644 ± 0.531

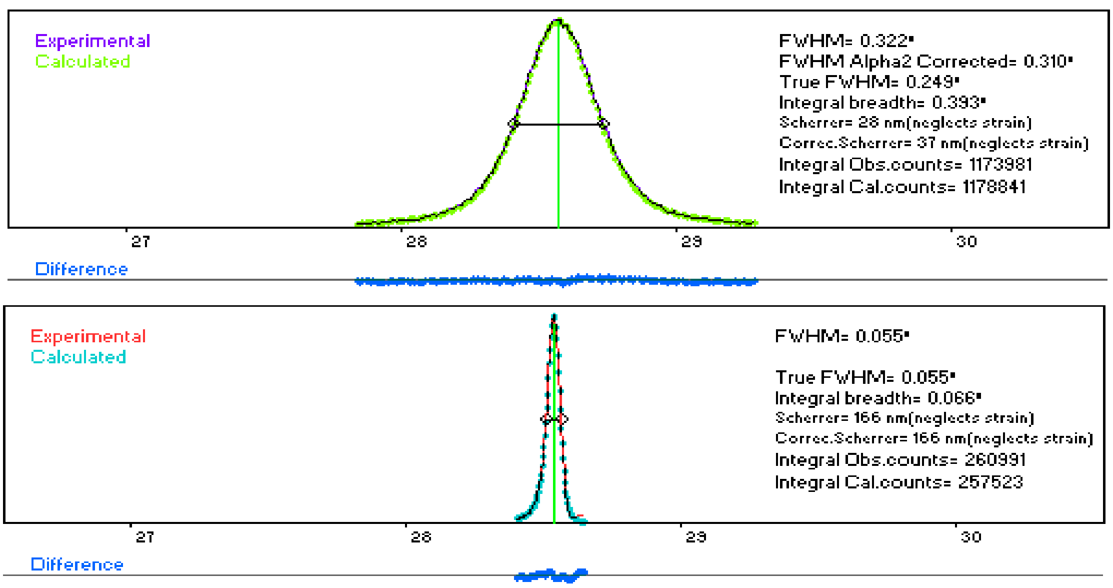

Figure 10.4. Powder individual profiles of CeO 111 reflection of low powder size (above) and large size (below) grains. The intensities of the latter are divided by 106 in order that they can be comfortably handled by the program. As will be seen below, there increase in the size of the mosaic is related to sample larger crystals (as evidenced by the decrease in the width of the profile). The $K\alpha_2$ component of radiation has been eliminated, to adjust the profile to a *pseudovoigt* function . .

Line broadening. The simplest measurement of dispersion (line breadth) is the a full width of the intensity distribution at half of the maximum intensity (*FWHM*). If the distribution is not symmetrical ***XPowder*** calculates the half of the maximum intensity on the left (w_1) and right (w_2) hand side of the peak ordinate. The *asymmetry* is defined as w_2/w_1. ***XPowder*** also includes the *integral breadth* β, defined as the width of a rectangle having the same area and height as the observed line profile. *Area asymmetry* (A_2/A_1) has similar sense with *asymmetry*, by using of the left (A_1) and right (A_2) hand side areas of the peak ordinate. The shape of the profiles is measured by the *shape factor* ϕ, defined as the ratio of the *FWHM* to the *integral breadth*. Thus, the calculated parameter for a profile are:

FWHM = Full width at half maximum.
Asymmetry = w_2/w_1
Integral breadth β
Area asymmetry = A_2/A_1
Shape factor ϕ = *FWHM* / β

The causes of the widening and shape of the profiles are:

- Instrumentals
  - 1. The radiation is not strictly monochromatic.
  - 2. Geometry and diffractometer optical. Instrumental function.

- Related to the specimen.
  - 3. High percentage of amorphous materials (high background).
  - 4. Mosaic size (*coherent domain size* in diffraction terms).
  - 5. Heterogeneities and distortions of the unit cell
  - 6. *Non Uniform Strain*' (or simply '*Strain*')

'*Non Uniform Strain*' (or simply '*Strain*') and '*Uniform Strain*' are two different concepts. The first cause a heterogeneous dispersion of the d-spacing values, resulting in a widening of different profiles in each θ. In the second type, the sizes of all the unit cells modifying alike, as for thermal expansion or Pascal pressure, which causes a non-lineal displacement of the 2θ angles of the reflections patterns, but not the widening of the profiles.

Of all these possible causes of widening the profiles, only the latter two are related to the nature of the analyzed crystals and are often referred as 'microtexture'. It is therefore necessary to find a suitable procedure to subtract the effects of the first three, which are alien to their own crystals, so that the shape of the 'pure profile', to say the profile due exclusively to that microtexture, will be isolate.

1. *Monocrhomatism*. Of course, acquire the patterns with monochromatic radiation through the use of serialized monochromators or synchrotron radiation is convenient. But this is not always possible, so in some methods of microtexture analysis (Scherrer analysis or Williamson-Hall) is needed, as a preliminary step, the complicated process of elimination of the $K_{\alpha 2}$ component (stripping). XPowder is done with sufficient quality through the push of the button . If the Williamson-Hall methods are used, the elimination of $K_{\alpha 2}$ also must be performed on the experimental *instrumental function* (see next item).
2. Instrumental function. The calculation of the so-called '*instrumental function*' is more complicated. This function describes the profile shape induced solely by the diffractometer, and that conditions at last, the final resolution of this technique. The *instrumental function* in theory can be calculated as the product of convolution of the curves generated by each of the components of diffractometer (X-ray source, the sample surface, divergence of the rotation axis, transparency of the speciment, set of divergence and reception slits , monochromator, etc). The details of this calculation can be seen in the book of HF Klug and L.E. Alexander, *'X Ray Diffraction Procedures*', whose 2nd edition has been printed by Wiley & Sons in 1974. In general this theoretical calculations are very complicated, because it is very difficult the parameterization of the functions of each element of convolution. Instead, experimental patterns of very high crystallinity compounds (B_6La, CeO, etc.)

are often used in order to uses as an *instrumental function.* Then, the *instrumental profile broadenig* can be modeling by the Caglioti equation:

$$B^2 = U \cdot \tan^2\theta + V \cdot \tan\theta + W + P/\cos^2\theta$$

Where B is the width of the profile for each pure angle θ. U, V, W and P have to be adjusted from the *very high crystallinity standard pattern (CeO, B_6La, Corundum,...)*. Other times and whenever possible, the *instrumental function* can be obtained from a sample that possesses not only a high crystallinity, but a similar composition to the studied specimen. In this case, the Caglioti function is tot used. The calculation of the Caglioti function is performed automatically by XPowder, as explained in Chapter 11.

3. Background. Some methods of microtexture analysis, using only the reflection widths (Scherrer and Williamson-Hall), needed to remove the background ( ) before making adjustments in the distribution functions of the crystal reflections. However, except in cases where it is really excessive, the background should never be removed. The background should never eliminated when using the of Warren-Averbach methods, of course

The distribution function that XPowder used to model the *pure profiles* (profiles cleaned of instrumental interference) is:

$$\mathbf{P(x) = \Phi_{(0)} \left\{ \gamma \cdot e^{-\pi x^2 [4 \cdot Ln2/\pi]/(B)^2} + [(1-\gamma) \cdot B^2/2(B^2+x^2)]^p \right\}}$$

Where:
x = free variable
B = Reflection broadening (refinable parámeter or experimental data)
γ and p are refinable parámeters
If $\gamma = 1$, p=0 the function is Gaussian
If $\gamma = 0$, p=1 the function is Lorentzian (or Cauchy)
If $\gamma = 0$, $p > 1$ Pearson VII
If $\gamma = 0$, $p < 1$ Super Lorentzian
If $\gamma = 0$ to 1, $p = 0$ Pseudo Voigt (Gaussian + Lorentzian)
If $\gamma = 0$ to 1, $p \neq 1$ Mixed function
$\Phi_{(0)}$ = Function value for x = 0 (maximum)

Asymmetry. XPowder adjusts, independently the right and left sides of the diffraction profiles, so it is possible to quantify the asymmetry of both, areas as B parameters.

With a strictly monochromatic radiation, sometimes, the slope of the profiles is softer towards minors 2θ angles. This can be attributed to a lack of uniformity in the size of the unit cell, due to partial hydration process that causes increased volume crystalline, by way of example.

If the slope is softer towards larger 2θ, the cause is more difficult to explain. Sometimes this can occur in the process of crystallization from a solid solution, in which the more modern cells are form from isomorphic elements of smallest radios. On the contrary, can be caused in the process of dissolution where the more soluble terms are largest radio elements. In any case, systematic measures from the parameters of asymmetry and form factor described above can be established.

Profile analysis methods based on width and shape of the diffraction profiles.

The use of strictly monochromatic radiation allows very simple treatments of profiles in terms of variance, so that when the profiles are adjusted to Cauchy functions, you can write:

$$B_{total} = B_{Instr} + B_{sample} = B_{Instr} + B_{size} + B_{strain}$$

If the profile function is Gaussian the relationship is as follows:

$$B^2_{total} = B^2_{Instr} + B^2_{sample} = B^2_{Instr} + B^2_{size} + B^2_{strain}$$

From the analysis of the *distribution function* used by XPowder, a more general relationship can be inferred for the *pseudo voigt*:

$$B^{(1+\gamma)}_{total} = B^{(1+\gamma)}_{Instr} + B^{(1+\gamma)}_{sample} = B^{(1+\gamma)}_{Instr} + B^{(1+\gamma)}_{size} + B^{(1+\gamma)}_{strain}$$

This equation allows easily deduce the value of the width of the reflections when this type of profile function is adequate. The refinable parameter $\boldsymbol{\gamma}$ is the Gaussian component of the voigt function which is automatically calculated by Xpowder

1. Scherrer Method.

It is used to calculate the coherent domain size (uncorrected strain) from a single reflection profile (λ supposed monochromatic):

$$\mathbf{Size(\mu m) = K \cdot \lambda(Å)/(10 \cdot B_{size} \cdot \cos\theta)}$$

The coherent domain size '**Size(µm)**' is often expressed in nanometers (hence the 10 that appears in the denominator). **λ (Å)** is the wavelength of monochromatic radiation and θ_o is the central angle of reflection.

The width of the reflection $\mathbf{B_{size}}$ can be *FWHM*, or the β *integrated width*, expressed both **in radians**. When the instrumental role is known, $B^{(1+\gamma)}_{sample}$ can be obtained by the suitable relationship $B_{sample} = B_{total} - B_{Instr} \approx B_{size}$. Otherwise, it can make a gross oversimplification assuming that $B_{size} \approx B_{total}$. **Strictly,** $\mathbf{B_{sample}} = \mathbf{B_{size}}$ **only for θ=0** (where B_{strain} =0, see below). **K** is a experimental constant (0.8>K>1.1), with different value when β instead *FWHM* is used. Optionally XPowder calculates this value but generally uses K = 1

To measure the size of the coherent domain with Scherrer method, XPowder use the button  or the Strain and X-size command of home menu. Once on the appropriate screen, press the left mouse button on , or click just about any reflection profile, and the automatic adjustment to a 'pseudo Voigt' function is obtained (γ is also fitted), as shown in Figure 8.4. It is desirable to make a proper $K\alpha_2$ stripping, and even an '*Spline*' interpolation, before starting the calculations. If you wish to obtain results expressed in absolute values, which can be compared with those of other laboratories, the *instrumental function* should also be set in advance. The background subtraction is not desirable to make, unless cases of very poor quality patterns. In any case, the background subtraction should not be too 'aggressive'.

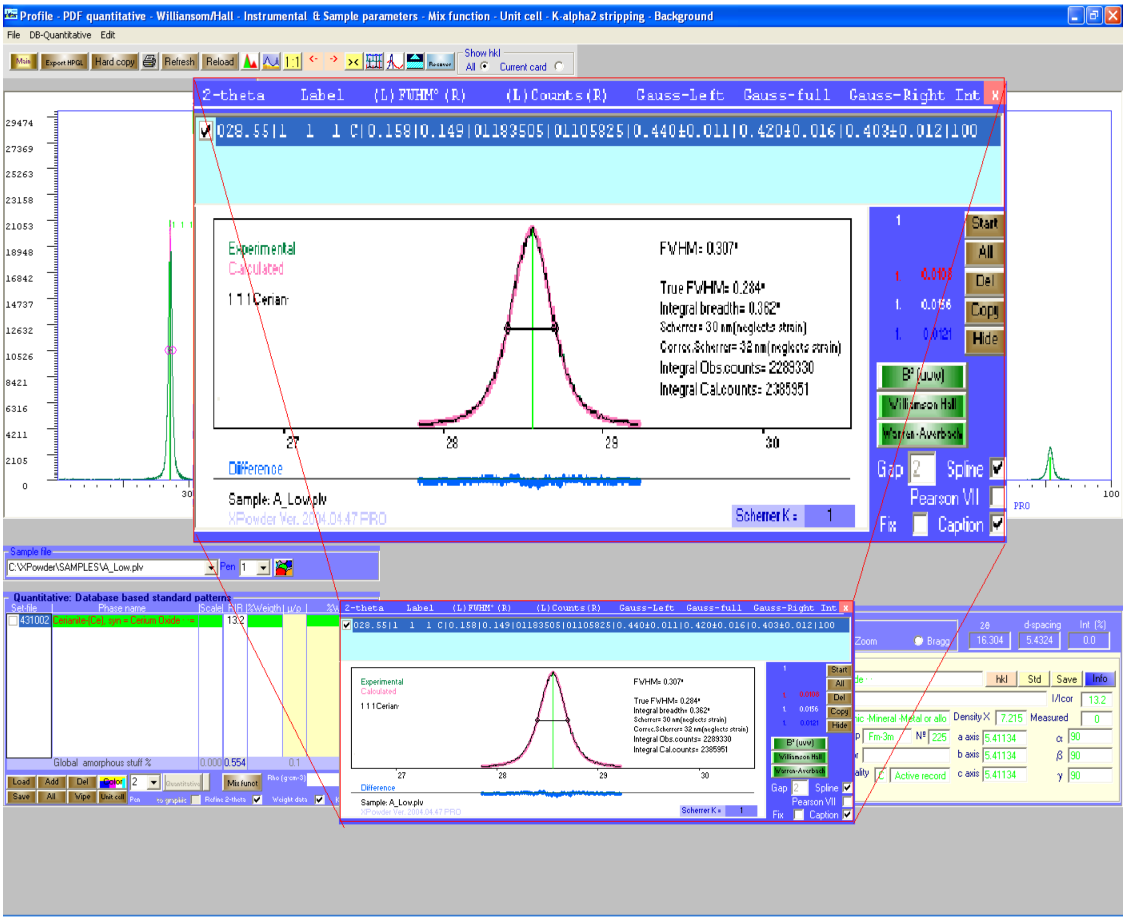

Figure 10.5.

The data shown in the figure 10.5 are as follows:

- 2θ of the maximum ('2-theta' column).
- If the object 'Matching' is present, *hkl* index are shown, on the contrary 2θ is printed. (Column 'Label').
- Values' FWHM 'expressed in degrees of 2θ, both to the right side (R) as to the left (L). Columns '(L)', 'FWHMº', '(R)'
- Gaussians components (γ) of the adjusted functions by the *Right* and *Left*, as well as the error of those values (Columns' Gauss-left ',' Gauss-full 'and' Gauss-Right '). The statistical values for left, full and right profiles are also shown to the right of the chart with red, white and blue respectively.
- Drawings of the adjusted and difference functions (blue).
- Drawing and value of experimental FWHM.
- Corrected FWHM Value for the instrumental function (True FWHM), that should be calculated for each diffractometer. In any case, the program uses latest available function.
- Integral Breadth in 2θº. Coherent domain size in nm without correction instrumental ('Scherrer'). K = 1 is used and the widening of the profile caused by 'Strain' is not taken into account.
- Idem with instrumental correction ('Corr Scherrer'). K = 1 is used and the widening of the profile caused by 'Strain' is not taken into account.
- Experimental profile integral counts (Integral Obs. Counts).
- Calculated profile integral counts (Integral Cal. Counts).

If the box Fix is marked, the position of the highest profile is set at the exact angle 2q, which has made the 'click' with the mouse. In another case, the program finds the position of the maximum.

If the box Pearson VII is marked, the exponent **p** of the general distribution function is refined.

If the box Spline is marked , the experimental data are interpolated virtually, through an a cubic spline, and the position of the maximum with more precision is obtained.

The box Gap contains the interval which will be used in adjusting the distribution functions, on both sides of the maximum.

If the box Caption is unchecked, any comments appear on the image.

The button Start allows you to start a new list of measures. It is used when switching experimental options, or at the beginning of adjustments for special functions such as those of Caglioti (for difractometer or sample), or Williamson-Hall microtexture analisys.

The button All lets you select all the profiles of the header list for subsequent calculations (Caglioti, Williamson-Hall, for example).

The button Del lets you remove the current profile of the list (blue stripe).

The button Copy moves the graphic to clipboard.

The button Hide hides the tool . It is the same as pressing the button  again.
.

El botón Rejet profile elimina de la lista general el último ajuste.

The button Rejet profile lets you remove the last fitted profile.

The button B^2[uvw] lets calculate the Caglioti equation. If the sample is a very high crystallinity specimen, enables you to adjust the instrumental function (see Chapter 11).

The button Williamson-Hall performs the calculation of the size of mosaic and '*Strain*', according to the method of Williamson-Hall.

The button Warren-Averbach is equivalent to , and go to a special display, where are the tools necessary to perform calculations of mosaic sizes and '*Strain*' by 'Warren-Averbach' methods, as well as '*Log-normal*' distributions. This button involves a reload of the original data of the diffractogram pattern, so that all operations carried out before will be cancelled (background subtraction, $K\alpha_2$ stripping, etc).

All the partial results are listed in detail in the *Log file* for each of the analyzed profiles, as shown in the following example:

```
-------------------------------------------------------------------
Profile Information Statistics (Parts of profile L= Left R= Right):
1  1  1 Cerian·
2-theta: 28.553 D-spacing= 3.1236
K-Alpha2 stripping has been performed
                                                ____________________________________
______________________________________________|     Pseudo-Voigt Gaussian Weigh    |____
2theta|  Label  |(L)FWHM°(R)| (L) Counts (R)  | Left part |   Full    |Right part | Int
028.55|1  1  1 C|0.158|0.149|01183505|01105825|0.440±0.011|0.420±0.016|0.403±0.012|100
_________________________________________________________________________________________
Observed FWHM= 0.3070 (2-theta°)
```

```
FWHM (After Instrumental Broadening Corrections)= 0.2838 (2-theta°)
Current Instrumental Cagliotti  Coefficients (x 10000):  U= 0.032900   V= -0.035600   W= 0.019030
Asymmetry= 0.9438
Areal Asymmetry: 0.9344
Integral breadth: 0.362 (2-theta°)
Shape factor (Observed FWHM/Integral breadth): 0.847
Max. counts: 21053
Uncorrected Size (Scherrer-neglects strain)= 29.7 nm. (Scherrer K=1)
K-Alpha2 and Instrumental Broadenig Corrected Size (Scherrer-neglects strain)= 32.1 nm. (Scherrer K=1)
Integral observed counts : 2289330
Integral calculated counts= 2385951
Pearson component has not been fitted for profile
```

2. Williamson-Hall Method .

The method of *Scherrer* explained above, uses a single X-Ray reflection for the calculations of mosaic size, but provides no information on the '*strain*' (ε), since this affects the profile differently in each 2θ value:

$$\varepsilon = B_{strain} / (4 \cdot \tan\theta)$$

$$B_{strain} = \varepsilon \cdot 4 \cdot \tan\theta$$

Where, B_{strain} is the variance of the distribution due to 'strain', expressed in radians, and ε is the 'strain' defined as $\varepsilon = \Delta L/L$. We note that the B_{strain} value is zero at the origin (θ=0).

The effect of '*strain*' on the broadening of the profile is generally very small compared to due to the magnitude of the mosaic. To correct the effect of '*strain*', the method of *Williamson-Hall* can be used.

The variance of a pseudo voigt distribution having γ Gaussian component can be expressed:

$$B^{(1+\gamma)}_{size} + B^{(1+\gamma)}_{strain} = B^{(1+\gamma)}_{sample} = B^{(1+\gamma)}_{total} - B^{(1+\gamma)}_{Instr}$$

The method of *Williamson-Hall* calculates separately, the size and the 'strain' by two or more orders of a reflection HKL, but gave no information on the size distribution, provided by the method of *Warren-Averbach* , which will be explained later. Thus,

$$B^{(1+\gamma)}_{sample} = B^{(1+\gamma)}_{size} + B^{(1+\gamma)}_{strain}$$

$$\text{Size}(\mu m) = K \cdot \lambda / (10 \cdot B_{size} \cdot \cos\theta) \qquad (\lambda \text{ in Å , B in radians })$$

By removing and replace the values of B_{size} and B_{strain}, we get:

$$B^{(1+\gamma)}_{sample} = \{K \cdot \lambda / [10 \cdot \text{Size}(\mu m) \cdot \cos\theta]\}^{(1+\gamma)} + \{\varepsilon \cdot 4\tan\theta \cdot \}^{(1+\gamma)}$$

By rearranging , we get

$$\{B_{sample} \cdot \cos\theta\}^{(1+\gamma)} = \{K \cdot \lambda / [10 \cdot \text{Size}(\mu m)]\}^{(1+\gamma)} + \varepsilon^{(1+\gamma)} \cdot \{4 \cdot \sin\theta\}^{(1+\gamma)}$$

This is the expression of the equation of a straight line **y = b + *a* ·x** , whose function values are **y=** $\{B_{sample} \cdot \cos\theta\}^{(1+\gamma)}$ and independent variables are **x=** $\{4 \cdot \sin\theta\}^{(1+\gamma)}$. If the experimental values **x** are plotted versus **y**, the absolute values of Size(μm) and ε can be obtained from the straight regression line.

In this way, for x= 0 we can obtain the value of ***b*** **=** $\{K \cdot \lambda / [10 \cdot \text{Size}(\mu m)]\}^{(1+\gamma)}$ and the slope is ***a*****=** $\varepsilon^{(1+\gamma)}$. From ***b*** and ***a*** we obtain Size(μm) and ε respectively.

As can be seen easily, the size obtained depends on the *hkl* direction and at least two observations are needed (eg 111 and 222). In isometric crystals can be used occasionally reflections from different directions, although the detailed analysis tends to give a much richer information.

With XPowder, this analysis is done via the button Williamson-Hall on the screen of the figure 10.5.

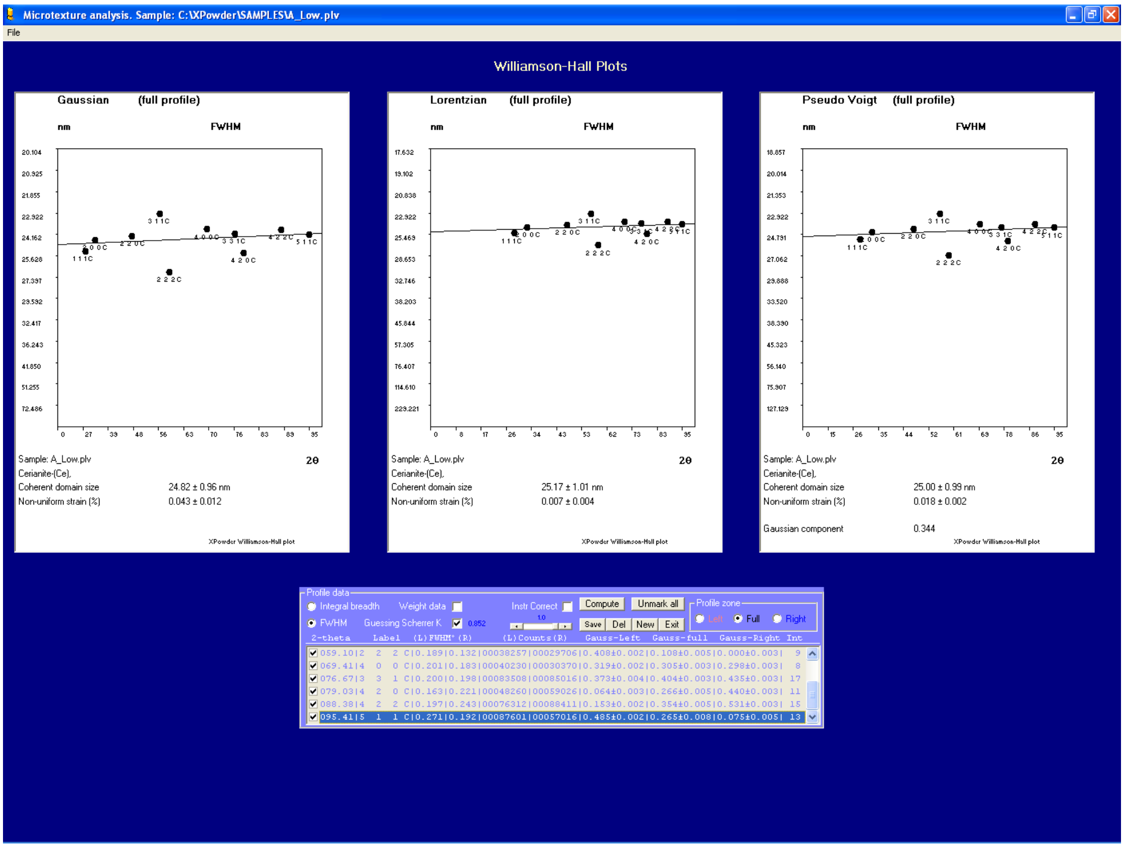

Figure 10.6.

The figure 10.6 shows an analysis of 106 *Williamson-Hall* made automatically on all reflections of a diffractogram of CeO. The three models correspond to Gaussians, Lorentzians and Pseudo Voigt models respectively. As broadening criterion has been used FWHM. The constant K value from *Scherrer* equation is optimized (K = 0.852) (box Guessing Scherrer K marked). The values of '*Strain*' are expressed in% and are very low, according to the values of the slope of the straight lines in all cases.

Other options such as (Integral Bread), (Weight data,instrumental correction (Inst.Corrc), right side, full side or left side profiles (selecting in the Profile zone framework, etc can be used.

Figures 10.7 y 10.8 show the *Williamson-Hall* analysis performed on the h00 reciprocal direction, with and without instrumental correction respectively.

Both the method of *Scherrer* as the *Williamson-Hall*, provide size values, as measured on directions HKL, whose calculations involved in the entire volume of crystalline domains. That is the criterion used for statistical weight is the volume. The term '*volume weighted*' is used to refer to the sizes obtained, as opposed to the ' *area weighted* ' provided by other methods such as the *Warren-Averbach* which is explained below. In general the weight methods based on '*volume*' provide values greater than those achieved with '*areas*'.

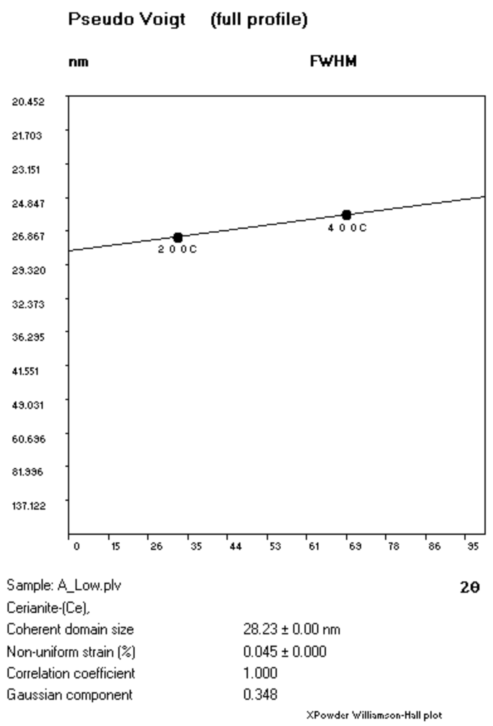

Figure 10.7. Williamson-Hall plot for the h00 direction. The instrumental correction was made.

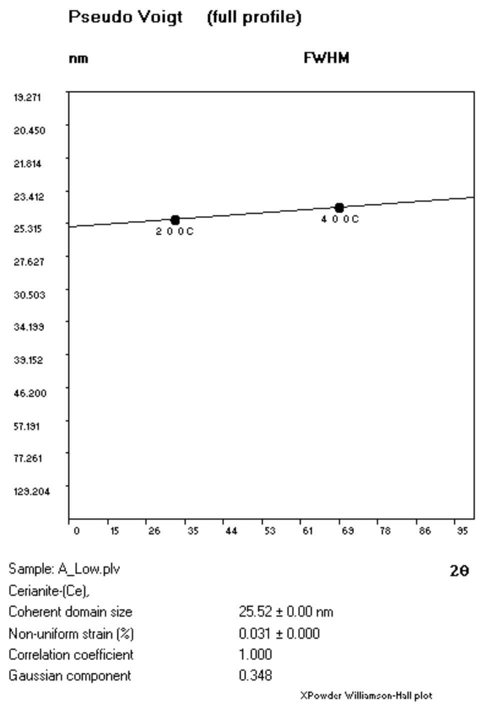

Figure 10.8. Williamson-Hall plot for the h00 direction. The instrumental correction was not done

Home

Warren-Averbach method.

A more comprehensive and accurate study of the diffraction profiles based on Fourier analysis, attends the role of total profile (R_{total}) as a result of the convolution of the instrumental profile (R_{Instr}) with the function generated by the sample (R_{sample}), being the latter the product of convolution of the size function (R_{size}) and due to strain function (R_{strain}).

$$R_{total} = R_{Instr} * R_{sample} = R_{Instr} * R_{size} * R_{strain}$$

The method requires the representation of diffractograms in reciprocal space, instead of doing it in classic 2θ function. Obtaining histograms diffraction in this space has very experimental difficult, as it requires appropriate programming of diffractometer very different than usual. XPowder uses an alternative path based on the theoretical calculationof histograms (ie diffractograms with $\Delta 2\theta$ constant) based on typical 2θ, (which is the usual way of presenting the data) through interpolation methods for cubic spline. It has been proven the effectiveness of this method that allows you to create reciprocal graphs with the same quality and form of profiles than those obtained experimentally. The method is used both for the instrumental function as to the sample function.

The *Warren-Averbach* method is a highly elaborated approach of size and strain analysis by powder X-Ray method which uses the deconvolution of the structural line profile (true profile) and the Fourier transform for evaluation of size of the coherent domain and strain (to say: space dispersion $\Delta d/d$ %). This methods states that the absolute values of Fourier cosine coefficients are then product of the size and the strain coefficients (Bertaut 1949). The coefficients can be numerically calculated and then related to the distribution of the column length (L), defined as the distance in the crystallite, perpendicular to the diffracting planes *hkl* (parallel to diffracting $\mathbf{q}_{hkl}$ vector). The convolution of the size broadened and strain broadened profiles in reciprocal space is the product of their Fourier transforms in real space. The absolute cosine fourier coefficients ($A_{L,q}$) of the true profile are:

$$A_{L,q} = {}^{s}A_{L} \cdot {}^{\varepsilon}A_{L,q} \qquad [1]$$

Being

${}^{S}A_{L}$ absolute cosine fourier coefficients size dependents,
${}^{\varepsilon}A_{L,q}$ absolute cosine fourier coefficients strain (ε) L and q dependents and
$q = 2\cdot\sin\theta/\lambda$

If two or more order of the reflection for hkl plane are available in the diffractogram, separate information for size and strain can be extracted assuming small strain values and Gaussian strain distribution for all values of L. Applying logarithms to [1]:

$$\mathrm{Ln}(A_{L,q}) = \ln({}^{s}A_{L}) + \ln({}^{\varepsilon}A_{L,q})$$
$$\approx \ln({}^{s}A_{L}) - 2\pi^2 L^2 q^2 \langle\varepsilon^2_{L}\rangle \qquad [2]$$

where ${}^{\varepsilon}A_{L,q} = e^{-2\pi^2 L^2 q^2 \langle\varepsilon^2_{L}\rangle}$ (theoretical expression value for ${}^{\varepsilon}A_{L,q}$) and $\langle\varepsilon^2_{L}\rangle$ is the mean-square strain for the correlation distance L.

In successive plots of $({}^{\varepsilon}A_{L,q})$ versus q^2 at fixed L values, ${}^{s}A_{L}$ are obtained from the intercept of the strain lines (at abscissa = 0) and ${}^{\varepsilon}A_{L,q}$ from the slope of the strain equations. Note that they are a strains coefficients curve for each q profile.

General procedure in W-A analysis .

1. The sample and instrumental profiles are normalized to maximum value=1 (figure 10.9.) and plotted in the reciprocal space with constant step (abscissa = $2\cdot\sin\theta/\lambda$, ordinates = counts, figure 10.10).

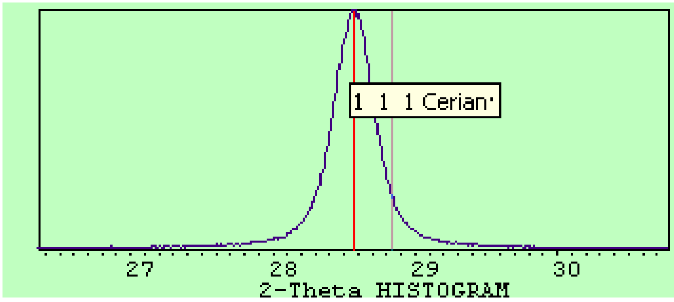

Figure 10.9. 2θ histogram.

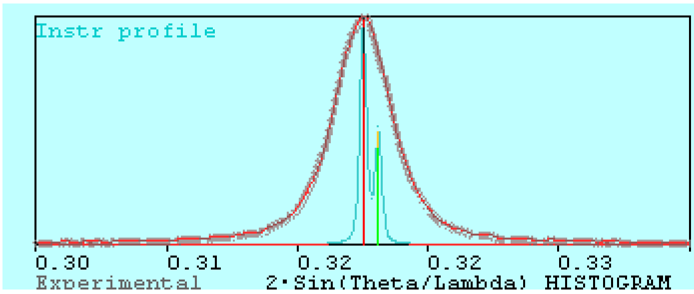

Figure 10.10. Reciprocal histogram

2. Deconvolution is carried out in order to obtain the ‘structure profile’ (‘pure profile’,’physical diffraction line’,…) of the sample pattern (figure 10.11).

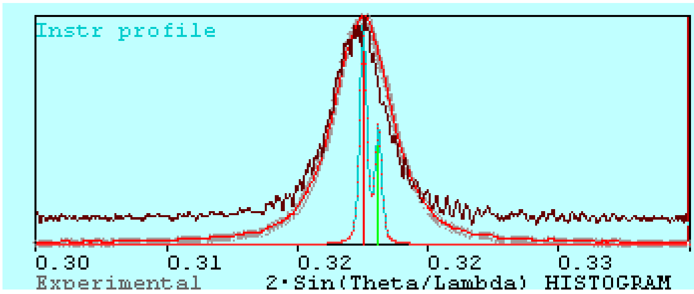

Figure 10.11.

3. Absolute values of cosine fourier coefficients (A_L) from the structure profile are calculated and normalized to A_0=1, and plotted versus column length L, perpendicular to the reflecting plane hkl (parallel to reciprocal q diffraction vector. Figure 10.12).

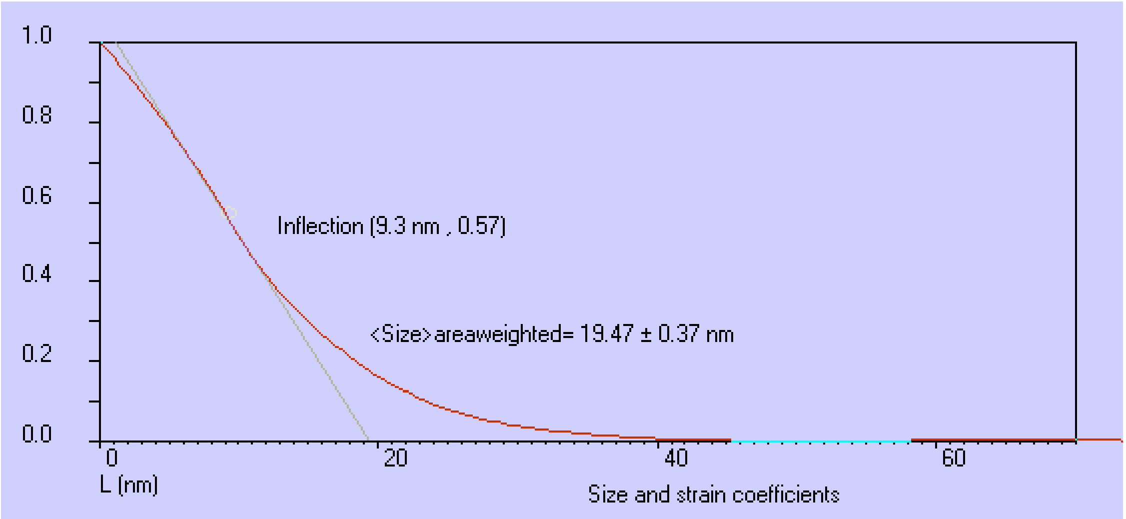

Figure 10.12

The average L_{AREA} size (uncorrected strain) is calculated from the tangent of the coefficients curve in ~~(A_0,0) point for A_L=0~~ in inflection point (2nd derivate=0, grey line in figure 10.12).

4. By selecting an upper Bragg's order line of hkl size and strain coefficients values can be separate, according to [2]

$$\ln(A_{L,q}) = \ln({}^{s}A_L) - 2\pi L^2 \langle \varepsilon^2 \rangle q^2$$

that is the straight line equation

$$y = b + a \cdot x$$

where

$b = \ln({}^{s}A_L)$
$a = -2\pi L^2 \langle \varepsilon^2 \rangle q^2$
$x = q^2$
$y = \ln({}^{s}A_L)$
${}^{S}A_L = e^b$ [3]
${}^{\varepsilon}A_{L,q} = \exp(aq^2)$ [4]
$\langle \varepsilon^2 \rangle = -a/2\pi L^2$ (average value) [5]

Then, it can be obtain the pure size Fourier-Cosine coefficients plot (column length probability to be greater or equal to L) and the average area weighted size value ($<L_{AREA}>$ = 20.07 nm in example) perpendicular to the (111) selected crystalline face (parallel to selected q reciprocal vector figure 10.13),

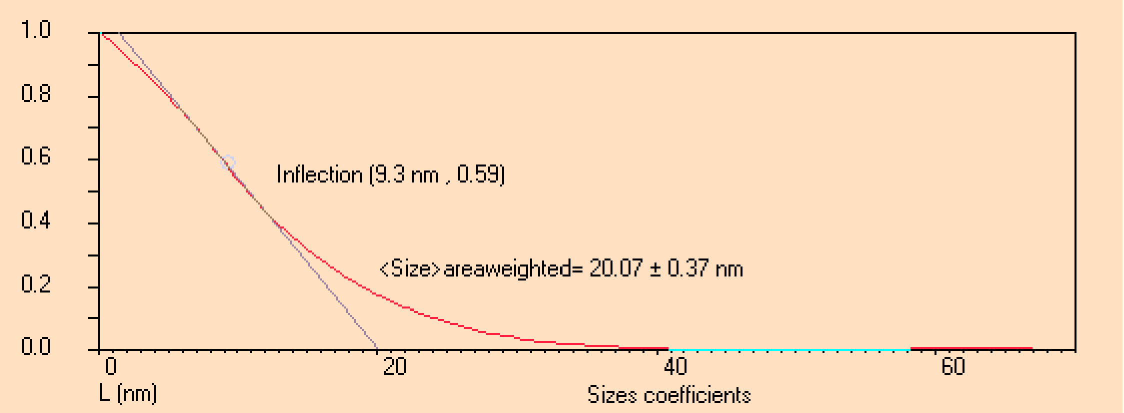

Figure 10.13.

the $^{\varepsilon}A_{L,q}$ strain Fourier-Cosine coefficients plots for each analyzed profiles (figure 10.14)

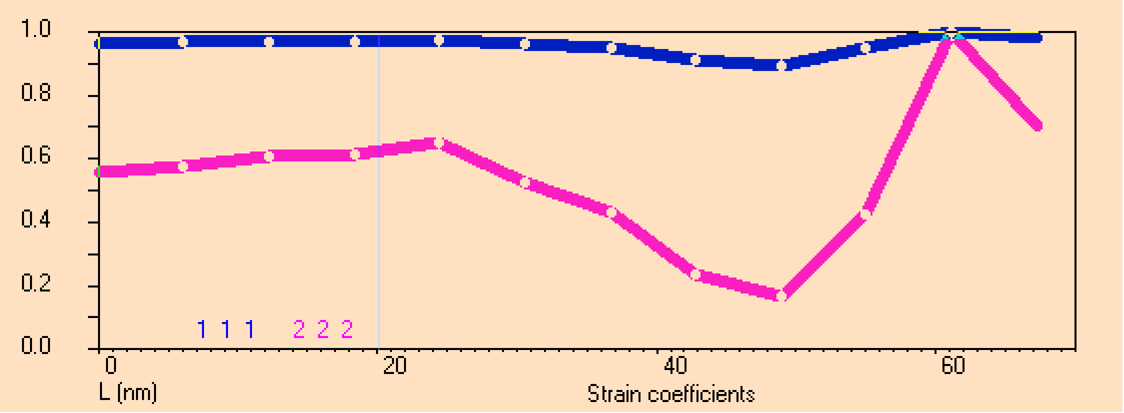

Figure 10.14

and the strain ($\delta d/d = <\varepsilon^2>^{1/2}$) versus column lengths plot (figure 10.15).

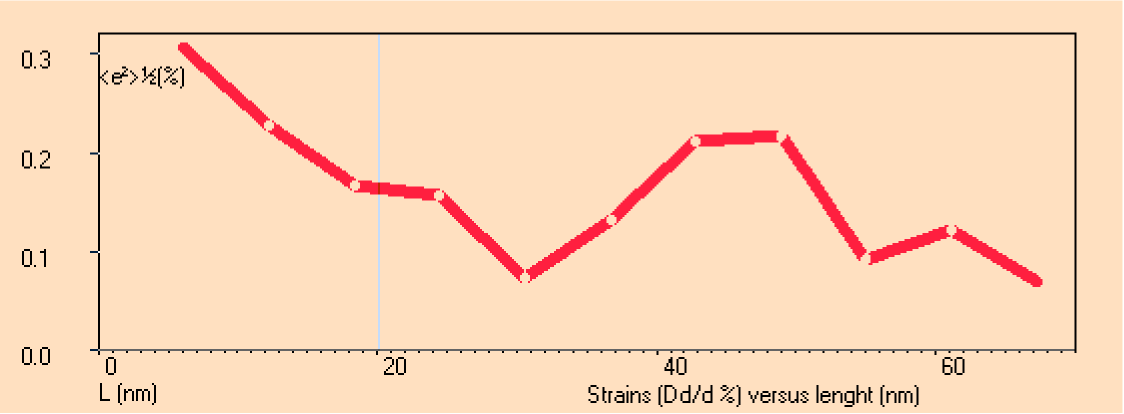

Figure 10.15

Log-normal distribution.

Additionally in most cases of small particles or nanocrystalline powder, it can be calculated then column length distribution by fitting to the log-normal distribution function (figure 10.16):

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma}\frac{1}{x}\exp\left\{-\frac{[\ln(x/m)]^2}{2\sigma^2}\right\} \qquad [6]$$

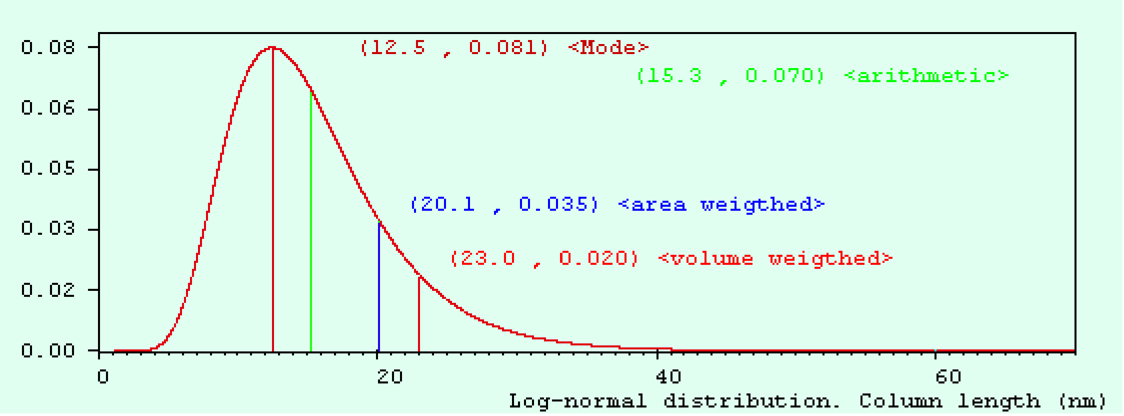

Figure 10.16

How does XPowder do this?

When a high quality diffractogram pattern is loaded, you can enter *to Warren-Averbach* module (figure 10.17) by clicking or Warren-Averbarch command of figure 10.5..

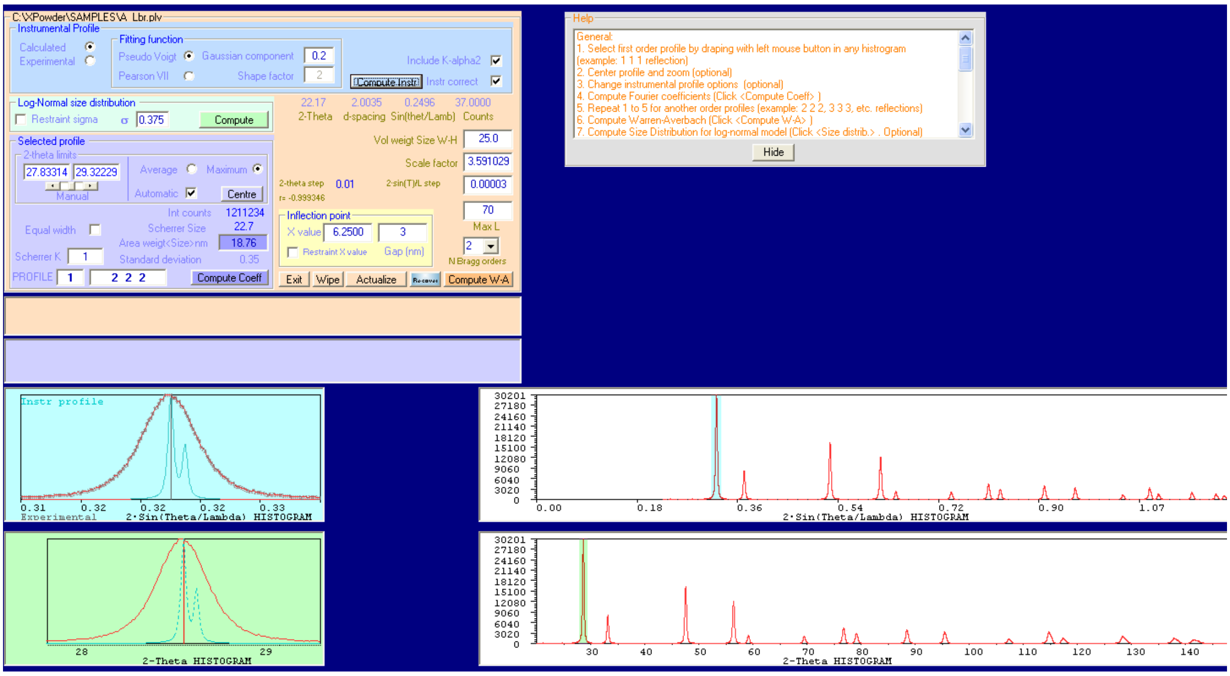

Figure 10.17.

Selecting profiles:

Select the profiles by draping around the reflection with the left mouse button in any histogram. The selected profile will be enlarged in the graphic with blue background (reciprocal histogram) and green background (2-theta histogram). Alternatively select 2θ lower and upper limit values and pulse **Actualize** **.** Optionally, use **Center** in order to improve the symmetry of the profile in the θ interval.

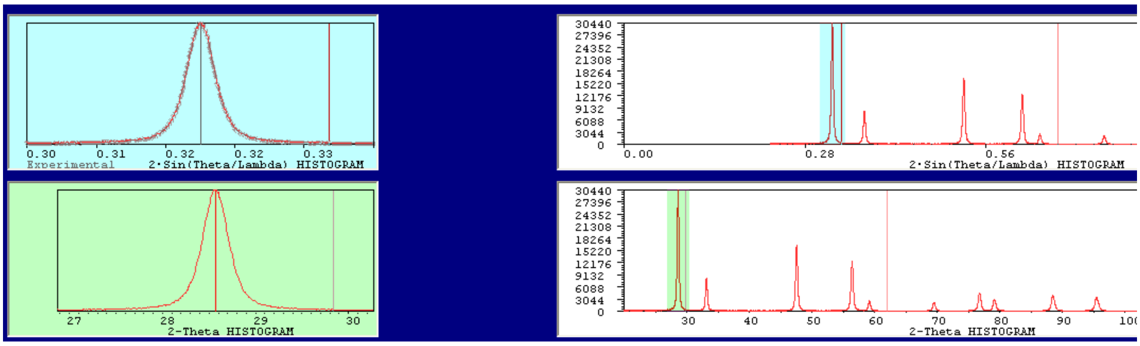

Figure 10.18.

Definable parameters and computation

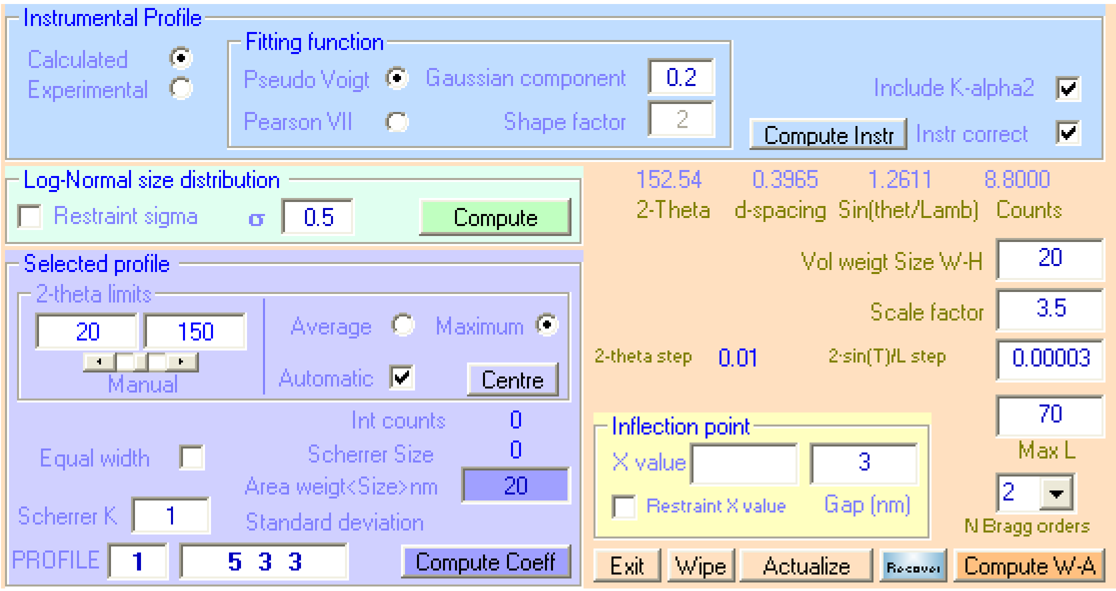

Figure 10.19.

Instrumental Profile section

Calculated: Allow calculate the instrumental profile by using the Caglioti approximation and selected distribution function (**Pseudo Voigt** or **Pearson VII**) by using an instrumental-standard sample (The National Institute for Standard and Technology- NIST, LaB_6 by example).

Experimental: Enable the use of a sample of equal composition and 'infinite' crystallinity for instrumental broadening effects correction.

Compute Instr. Shows the selected instrumental profile.

Include K-alpha2: The effects of the doublet $K\alpha_{1-2}$ will be corrected if checked.

Instr correct: The instrumental correction will be applied if checked. Default is 'Checked'.

Log normal size distribution section

Restraint sigma: Bind σ to actual value
σ: Dispersion for log normal distribution. If **Restraint sigma** is checked the σ value is not calculated.
Compute (or Hide) Log-Normal size distribution: Compute/Hide log-normal size analysis [7] and draw graphic of probabilistic distribution of L values (figure 8). The parameter used are $\mathbf{L_{area}}$ and σ.

Selected Profile section

2-theta limits: Lower and upper 2-theta of the selected reflection. The values can be input directly, by using of the displacement bar or by draping in the histograms.

Centre : The reflection is placed in the centre of the selected interval according to the **average** or the **maximum** of the profile. It will be automatically executed when **Compute_Coeff** are clicked and the **automatic** box is checked.

Maximum or **Average**: Criteria for automatic centering of the profile

~~**N polynom**: Select de order of the polynomium for fitting the column length L_{AREA}. Default value is 3.~~

~~**Points**: Number of cosine coefficients to be included in polynomial regression (A_0 to A_{points}). Default value is 10.~~

Equal width: Restraint to be equal the width of all the profiles. This box is checked automatically when the first profile has been analyzed by **Compute Coeff**.

Area weigt<Size> nm : Value of the area-weighted column length (L_{AREA} nm) for current analysis (both corrected or uncorrected strain)

Scherrer Size : Value of Scherrer size in nm for the current profile.

PROFILE n: Ordinal number of the actual profile

h k l: Editable label for actual profile.

Compute Coeff: Compute **Centre** (if the centre box is checked)**,** **Actualize** and the average area weigthted L_{AREA} size (uncorrected strain) is calculated from the tangent of the coefficients curve in (A_0,0) point for A_L=0 (figure 4). Uses [7], ~~**N polynom** and **Points** parameters~~.

Inflection point section

X value: Centre for <Size>$_{AREA}$ calculation

Gap (nm). Interval of X value for lineal regression in orden to obtain then <Size>$_{AREA\ WEIGHTED}$ value

Restraint X value: Bind **X value** to actual value.

Others parameters and commands

Max L: Upper limits in nm for column length in graphics. Default value is 45 nm.

Size W-H Estimated volume weighted size (nm). This value can be improved from XPowder Williamson-Hall plot module and can be changed manually by the user. It is used in the calculus of **σ.**

Recover Allow to recoup prior searching PDF2 cards. It is uses for get hkl index of the histograms reflections by stopping the mouse cursor on the graphics. By stopping in the reciprocal histogram profile, 'hkl' index of the reflection is writing automatically in the '**h k l'** editable label box.

N Bragg order Allow to show the first N reflection orders from the actual position of cursor.

2·sin(T)/L step Editable value of the step in reciprocal histogram. The change must be actualized with the button **Actualize**.

Wipe Reset profile counter and analytical results.

Actualize Compute and redraw graphics according to actual parameters. It will be automatically executed when **Compute Coeff** is clicked.

Exit Leave Warren-Averbach tools and go to XPowder home screen.

Compute W-A: Execute [1] to [5] Warren-Averbach analysis and draw figures 4 to 7. Uses the profiles selected by checking in the list box of figure 12.

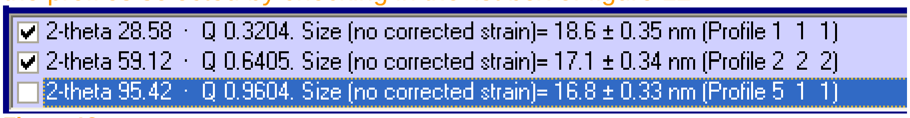

Figure 12.

Note: Use right mouse button for others pop-up contextual menus. **Help** button shows a quickly W-A user guide.

Warren-Averbach Quick Start User Guide

1. Select first order profile by draping with left mouse button in any histrogram (example: 1 1 1 reflection).

2. Centre profile and zoom (click Centre. Optional).

3. Change instrumental profile options (optional).

4. Compute Fourier coefficients (Click Compute Coeff).

5. Repeat 1 to 5 for another order profiles (example: Select 2 2 2, 3 3 3, etc. reflections)

6. Compute Warren-Averbach (Click Compute W-A)

7. Compute Size Distribution for log-normal model (Click Size distrib. Optional)

Lectures.

Balzar, D., Audebrand, N., Daymond, M.R., Fith, A., Hewat, A. Langford, J.I., Le Bail, A., Louër,D., Masson, O., McCowan, C.N., Popa, N.C., Stephens, P.W. and Toby, B.H. (2004) *J. Appl. Cryst*. **37**, 911-924

Bertaut, E.F. (1949). *C. R. Acad. Sci. Paris*, **228**, 187-189, 492-494.

Warren, B.E. *X-ray Diffraction*. (1969). Reading, Mass. Addison-Wesley. 1990 Edit. 381 p.

Lucks, I., P. Lamparter, E.J. Mittemeijer, *An evaluation of Methods of Diffraction-Line Broadening Analysis. Appliedto Ball-Milled Molybdenum*, J. Appl. Cryst. **37**(2004) 300.

Home

Chapter 11. Caglioti equation.

The Cagliotti equation calculates the width of the diffraction peaks (B), through the adjustment of the three parameters (U,W,W,P) of the formula:

$$B^2 = U \cdot \tan^2\theta + V \cdot \tan\theta + W + P/\cos^2\theta$$

In principle, this function was used to synchrotron diffraction, but also can be used with any other of X-ray monochromatic radiation. There must have an efficient monochromator or eliminate analytically $K\alpha_2$ component, so that the function of Caglioti can be used correctly. $K\alpha_2$ stripping can be done by XPowder with enough precision, where values of wavelengths and reason $IK\alpha_2$/ $IK\alpha_1$ are sufficiently accurate. (See Chapter 3.4).

To adjust these parameters (U,V,W,P), we have to calculate individual profiles, as explained in Figure 10.4 and then, press the button $B^2(uvw)$. The image of the Figure 11.1 will be obtained.

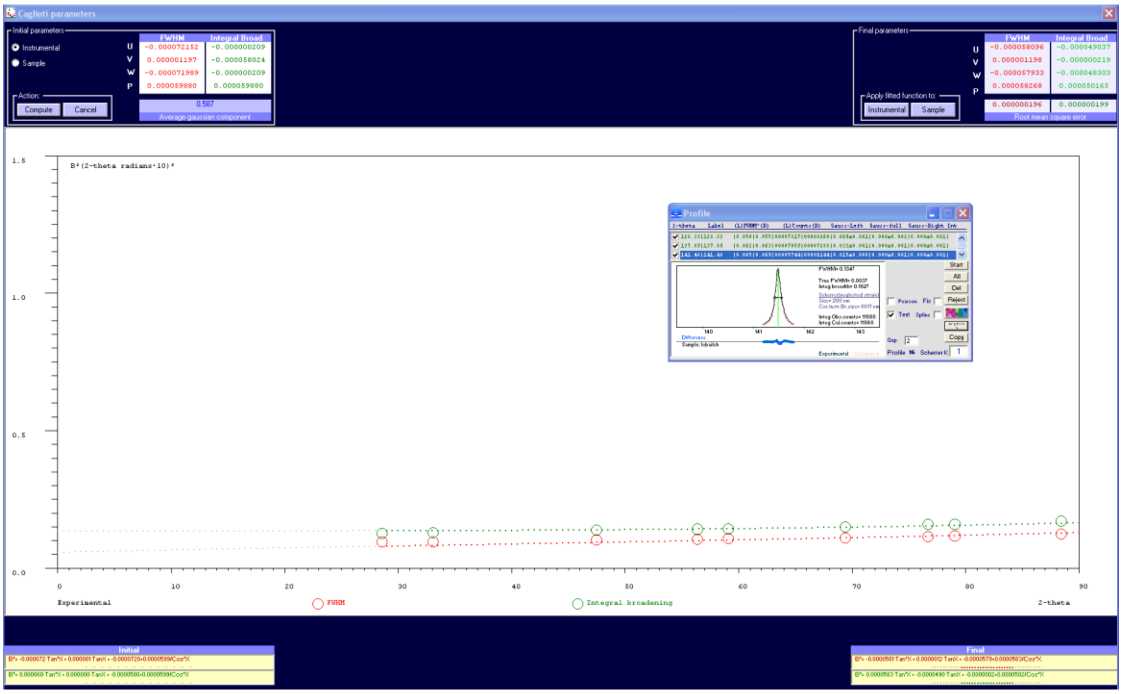

Figure 11.1.

In the graphof figure 11.1, the values of experimental widths and initial Caglioti functions are shown (Red circles= FWHM, Green circles= Integral broadening), both in algebraic and graphic form (the last one previously saved on the hard drive of your computer). You can adjust both the '*instrumental function*' (when using a standard sample of a very high crystallinity), as the '*sample function*' which can be used latter in theoretical profile calculations , or initial profile data in Rietveld analysis programs. Before making the Caglioti adjustments, XPowder automatically calculated the 'pseudo-voigt' average profile of the sample, whose Gaussian component appears in the top frame.

In this example, the Instrumental option must be chosen, because we want to adjust the *instrumental function* of the difractometer. Pressing Compute functions are calculated and adjusted for FWHM (red) and 'Integrated broadening' (green, Figure 11.2).

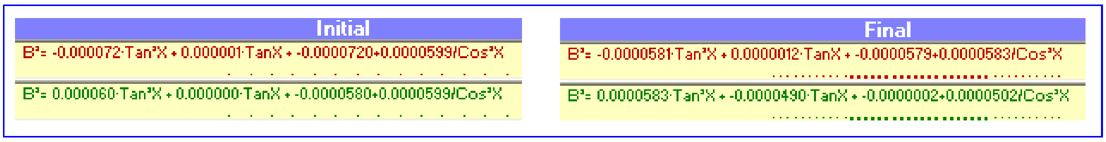

Figure 11.2.

The least-squareadjusted functions are drawn with thick points in the analyzed 2θ interval and with thin points in the extrapolated zones. The numerical values are printed on the bottom right. If it is then pressed Cancel, the calculations will be discarded.

▪ If Instrumental is pressed, the calculated values will be applied to all instrumental corrections which are required in the future. Alos, the file 'Xpowder.ini' (or 'XPowder12.ini') is updated:

[Profile]

InstrumentalU-Width= -0.000072152 *(for FWHM)*
InstrumentalV-Width= 0.000001197
InstrumentalW-Width= -0.000071989
InstrumentalP-Width= 0.000072325

InstrumentalU_WidthIB= -0.000058756 *(for integral broadening)*
InstrumentalV_WidthIB= -0.000000209
InstrumentalW_WidthIB= -0.000058024
InstrumentalP_WidthIB= 0.000059880

U,V,W and P parameters can also be manually entered into 'Xpowder.ini' (or into 'XPowder12.ini').

▪ Touching Sample, the UVWP calculated values will be applied to new theoretical profile calculations (for example when , by using 'Matching', you want to subtract from the experimental pattern, a identified partial profile in order to explore comfortably the rest of compounds. Auxiliar file 'Broad.txt' is now generated.

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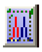
Chapter 12. Additional files.

XPowder.ini

It is a text file, which contains basic information about the initial configuration of the program. Can be modified through a text editor. Some data is updated from the XPowder program itself. The following example in green, it commented line by line (right in red).

[Xpowder]	Head
SampleDir= .\samples	Sample subdirectory in the directory program.
LoadFilterIndex= 2	Specifies the initial sample file format (1=All, 2=PLV, 3=Raw, 3=RD, 4=X'Pert, 5=Udf, etc.)
SaveFilterIndex = 1	Output data format files. All values are not valid.
DiagramForeColor= &HFF00FF&	Background color of main diffractogram in hexadecimal.
currentLd= Cu , 1.540598 , 1.54433 , 1.39217 , 0.5	Default anode: Element of anode, λKα1, λKα2,λKβ, IKα2 / Ikα1
lambda= Cr , 2.28970 , 2.29351 , 2.08480	Normalized λ values: Anode, λKα1, λKα2,λKβ
lambda= Fe , 1.93604 , 1.93991 , 1.75653	Idem
lambda= Co , 1.78897 , 1.79278 , 1.62075	Idem
lambda= Ni , 1.65784 , 1.66169 , 1.50010	Idem
lambda= Cu , 1.5405981 , 1.54433 , 1.39217	Idem
lambda= Mo , 0.70930 , 0.713543 , 0.63225	Idem You can modify or add radiation
lambda= Ag , 0.559363, 0.563775 , 0.49701	Idem
lambda= W , 0.208992, 0.213813 , 0.184363	Idem
lambda= Cu2 , 1.5405981 , 1.54433 , 1.39217	Idem
lambda= Dummy, 1.5405981 , 1.54433 , 1.39217	Idem
lambda= Synchrotron, 1.5406, 1.5406, 1.5406	Idem for Synchroron radiation (The three values must be equal).
kalphaFT= 1	Parameter used in the Fourier filtering. There should be no change
hRoller= 1	Horizontal initial value of 'roller' in 2θ°, for background subtraction.
vRoller= 5	Idem vertical in % counts.
interpolate= 2	Initial number of points to be interpolated by spline.
2-theta_Tuner= 0.1	maximum Δ2θ° for L.S. fifting in searching (0< Δ2θ° <0.4)
QUAntitative= True	Establishing the capacity to make quantitative analysis based on RIR
Amorphous_Whole_RIR= 0.5541791	Pseudo RIR global amorphous. Updates itself, according to the types of samples.
Monochromator_Constant= 1	Monochromator constant
rZoom= 50	Number of horizontal points of the window Zoom
iZoom= 50	Idem vertical
peakSearchMinInt= 4	Minimun initial intensities (%) in 'Searching'
peakSearchSmoo = 0.2	Inital smoothing of maximum in 'Searching'
SkipDuplicatePDF= False	If True: 'Searching' shows the better solutions from equal phases
[Initial PdfSubfiles]	Next instructions are for PDF subfiles
Deleted pattern= True	If True, Deleted PDF patterns are included in'Searching'
Inorganic= False	If True, 'Inorganic' PDF patterns are included in searching..
Organics= False	Idem 'Organic'
Mineral= True	Idem 'Minerals'
MetAl= False	Etc. Can be modified from running XPowder
CP= False	Idem
NBS= False	Idem
FORensic= False	Idem
EDUcational= False	Idem
ZEOlite= False	Idem
EXPlosive= False	Idem
SCMaterial= False	Idem
CEMent= False	Idem
CORrosive= False	Idem
POLymer= False	Idem
DETergent= False	Idem
PIGment= False	Idem
PHArmaceutical= False	Idem
ICSD= False	Idem
Ceramics= False	Idem
[www]	URL and e_mail of Xpowder:
XPowderSite= http://www.XPowder.com e_mail:support@xpowder.com	
InstrumentalU-Width= 0.000003290	Current value (U) of the Caglioti for function instrumental FWHM
InstrumentalV-Width= -0.000003560	Current value (V) of the Caglioti for function instrumental FWHM
InstrumentalW-Width= 0.000001903	Current value (W) of the Caglioti for function instrumental FWHM
InstrumentalU_WidthIB= 0.000003714	Current value (U) of the Caglioti for function instrumental Integral broadening
InstrumentalV_WidthIB= -0.000003341	Current value (V) of the Caglioti for function instrumental Integral broadening
InstrumentalW_WidthIB= 0.000002228	Current value (W) of the Caglioti for function instrumental Integral broadening
Rem OldUValue= 0.000044	The lines that begin with REM are not read by the program.

Std.txt

This file contains standard patterns and is used when you run the ' Edit-> Set 2-theta offset' or push  from the home screen in order to correcting instrumental 2θ misalignment. Each standard begins with the key '*Begin standard*", after the chemical symbol for the element of used anode, the name of the compound and a list of 2θ and intensities in scale thousand (separated by commas). The end of each pattern is a row with the key 000.0000,000. The first of the patterns whose name is 'None', lack of data and its presence is necessary, as in the following example:

```
Begin standard
Lambda= Cu
None
000.0000, 0000

Begin standard
Lambda= Cu
Sodium Choride (Halite syn)
027.3024, 0130
031.6547, 1000
045.3954, 0550
053.7887, 0020
056.4108, 0150
066.1488, 0060
072.9777, 0010
075.2129, 0110
083.8708, 0070
090.2991, 0010
101.0693, 0020
107.6764, 0010
109.9103, 0030
119.3563, 0040
127.0104, 0010
129.7306, 0030
142.0569, 0020
000.0000, 0000

Begin standard
Lambda= Cu
Calcium carbonate (Calcite Syn)
022.9948, 0120
029.3704, 1000
031.3808, 0030
035.9231, 0140
039.3546, 0180
043.0940, 0180
047.0672, 0050
047.4328, 0170
048.4552, 0170
056.4865, 0040
057.3326, 0080
058.0049, 0020
060.6048, 0050
060.9139, 0040
061.2713, 0030
062.9841, 0020
064.6004, 0050
065.5200, 0030
069.1476, 0010
070.1536, 0020
072.7817, 0020
073.6395, 0010
076.2077, 0010
077.0839, 0020
080.8346, 0010
081.4486, 0030
082.0136, 0010
083.6656, 0030
084.6848, 0010
086.3782, 0010
092.9588, 0010
094.5853, 0030
094.8949, 0040
096.0477, 0020
097.5282, 0010
099.0396, 0020
102.1170, 0010
102.8261, 0010
103.7715, 0010
103.9963, 0030
105.7159, 0020
106.0151, 0040
107.2017, 0010
109.4260, 0020
110.3477, 0020
000.0000, 0000

Begin standard
Lambda= Cu
Silicon(1)
039.8796, 1000
046.3690, 0250
067.7484, 0200
081.6145, 0200
086.1906, 0100
104.2542, 0030
118.8626, 0100
124.2775, 0100
150.8580, 0070
000.0000, 0000

Begin standard
Lambda= Cu
Silicon(2)
028.4106, 1000
047.2499, 0550
056.0584, 0300
069.0537, 0060
076.2928, 0110
087.9290, 0120
094.8431, 0060
106.5978, 0030
113.9622, 0070
127.4020, 0080
136.7419, 0030
000.0000, 0000

Begin standard
Lambda= Cu
Calcium Fluoride (Fluorite Syn)
028.2350, 0920
032.7239, 0010
046.9516, 1000
055.7016, 0330
058.4099, 0010
068.5964, 0100
075.7643, 0090
078.0951, 0010
087.2734, 0170
094.1097, 0070
105.6840, 0040
112.9358, 0060
115.4390, 0010
126.0590, 0080
135.0546, 0030
138.3980, 0020
000.0000, 0000

Begin standard
Lambda= Cu
Aluminum (Syn)
038.4720, 1000
044.7380, 0471
065.1333, 0219
078.2271, 0239
082.4352, 0071
099.0783, 0021
112.0410, 0082
116.5600, 0080
137.4500, 0081
000.0000, 0000

Begin standard
Lambda= Cu
Corundum
025.5760, 0720
035.1498, 0980
037.7672, 0440
041.6834, 0010
043.3402, 1000
046.1754, 0020
052.5480, 0480
057.4981, 0960
059.7375, 0030
061.1238, 0040
061.3031, 0090
066.5144, 0380
068.2018, 0570
070.4114, 0011
074.3001, 0010
076.8727, 0017
077.2342, 0010
080.4151, 0012
080.6922, 0070
083.2078, 0010
084.3481, 0050
085.1346, 0010
086.3465, 0040
086.4996, 0040
088.9972, 0080
090.7050, 0021
091.1794, 0100
094.8164, 0010
095.2357, 0190
098.3804, 0020
101.0638, 0140
102.8171, 0010
103.3008, 0031
104.6351, 0010
109.5222, 0010
109.8503, 0010
110.8154, 0010
110.9755, 0040
114.0680, 0030
116.0804, 0130
116.6098, 0100
117.8378, 0080
000.0000, 0000

Begin standard
Lambda= Cu
Quartz low (1)
020.8264, 0220
026.6217, 1000
036.5006, 0080
039.4111, 0080
040.2379, 0040
042.4168, 0060
045.7572, 0040
050.0838, 0140
050.5537, 0010
054.8066, 0040
055.2655, 0020
057.1730, 0010
059.8804, 0090
063.9282, 0010
065.6859, 0010
067.6728, 0060
068.0531, 0070
068.2451, 0080
073.3786, 0020
075.5847, 0020
077.5737, 0010
079.7871, 0020
079.9552, 0010
081.0554, 0030
081.3796, 0030
083.7256, 0010
084.8748, 0010
087.3647, 0010
090.7551, 0020
092.7170, 0010
094.5576, 0010
095.0107, 0010
096.1174, 0010
098.6254, 0010
102.0830, 0010
102.4429, 0010
103.7659, 0010
104.0809, 0010
106.0248, 0010
000.0000, 0000

Begin standard
Lambda= Co
Quartz    · · (79-1906)
024.2697, 0148
031.0354, 1000
042.7044, 0129
046.1689, 0067
047.1493, 0009
049.7232, 0037
053.7215, 0062
000.0000, 0000

Begin standard
Lambda= Co
Silicon    · (77-2108)
033.2200, 1000
000.0000, 0000
```

Note: The last two standard patterns have been created in the example from the Xpowder program itself from PDF2 records, for tubes with anode of cobalt. This involves first obtaining the different 2θ angles of the respective reflections, using the formula with the value of Bragg wavelength described in the database information. Subsequently, these values are normalized to the exact wavelength, for the same anode defined in the XPowder.ini file (eg currentLd = Cu, 1.540598, 1.54433, 1.39217, 0.5).

There are commercial programs that do not perform this normalization of λ and can cause during the operation of correcting, 2θ zero shift higher than the value that is tried to correct. In any case, what is more correct to directly enter the values of 2θ angles and intensities, observed directly on experimentas patterns obtained in well aligned diffractometers.

Favorites.txt

This file is used rarely, but it remains by compatibility with very primitive versions of the program. They have fixed text format and aims to quickly find specific records of databases through names, nickname or improperly written words. Each line contains the file (2 digits), a space, the number of the card (file, 4 digits), a space and all the familiar names or aliases in any language.

```
12 1234 set=two digits    file=four digits
## #### key words
33 1161 Cuarzo Quartz
 5  586 Calcita Calcite Calcium carbonate
36  426 Dolomita Dolomite
41 1475 Aragonito aragonite
33  268 Vaterita Vaterite Baterita
 5  593 Celestina Celestine
29  696 Siderita siderite
35  496 Fluorapatito Fapatito
 9  432 Hidroxiapatito Hapatito
 5  628 Halita sal gema sal comun halite
 6  263 Moscovita Muscovite
33  664 Hematites ocre
17  541 Weddellyte Weddelita Wedelita Wedellita
33  311 Yeso Gypsum
```

SolSol.txt

It is a text file containing the final stages of isomorphic series that can be used to interpolate chemical compositions. Data from each phase are written on successive lines:

Phase name, eje a, eje b eje c, α, β, γ

```
Calcite
4.9963
4.9963
17.1092
90
90
120
Dolomite
4.808
4.808
16.055
90
90
120
Magnesite
4.646
4.646
15.139
90
90
120
Forsterite
4.752
10.192
5.978
90
90
90
Fayalite
4.815
10.4597
6.0818
90
90
90
```

Default.cnf

It contains the initial communication parameters and configuration of Philips PW1710/00/12 devices. It is only necessary in the PLUS version.

```
[PW1712]
[Diffractometer communication port]
CommPort = 1
BaudRate = 9600
DataBits = 8
StopBits = 1
Parity = N
[Scan parameters]
ScanMode = CONTINUOUS
StartAngle = 3
EndAngle = 80
StepScan(2 - theta°) = .040
IntegrationTime(sec) = 0.4
ScanRate(2 - theta° / sec) = 0.1
Batch_mode= 0
[Pulse height analyzer]
LowerLevel = 35
UpperLevel = 70
[Diffractometer setting]
Monochromator= Graphite 2°
Filter= None
Slit_1 = AUTOMATIC
ReceivingSlit = 1/0.1/1
AutomaticSamplerChanger = PW 1775
Rem PW 1775,No,  ...
Spinner= PW 1774
Rem PW 1774, No
ThermoController = Comm3:9600,N,8,1
Rem  False / Comm3:9600,N,8,1
MaxTemperatureCentigrade= 250
GraphicRecorder = PW 8203A
Rem  PW 8203A,  PW 8203, NO
SingleGobelMirror = NO
GeneratorVoltage(Kv) = 40.00
TubeCurrent(mA) = 40.00
Stand_by_2theta = 5.00
DiffractometerSite= <<To be personalized>>
[Profiles]
01 Profile 026.00 003.00
02 Profile 035.00 003.00
03 Profile 044.00 003.00
04 Profile 000.00 000.00
05 Profile 000.00 000.00
06 Profile 000.00 000.00
07 Profile 000.00 000.00
08 Profile 000.00 000.00
09 Profile 000.00 000.00
10 Profile 000.00 000.00
11 Profile 000.00 000.00
12 Profile 000.00 000.00
```

Other specific '*.cnf' files can be created for particular applications, through editing 'default.cnf', or using the 'File-> Save Setup file', in the acquisition diffractograms module. Also it can be used 'Load Setup file' in same module.

Home

Chapter 13. Data collection from the diffractometer.

This option is available in the version **XPowder *PLUS*** for the PW 1700/10 diffractometers through a PW1712 serial dual interface.

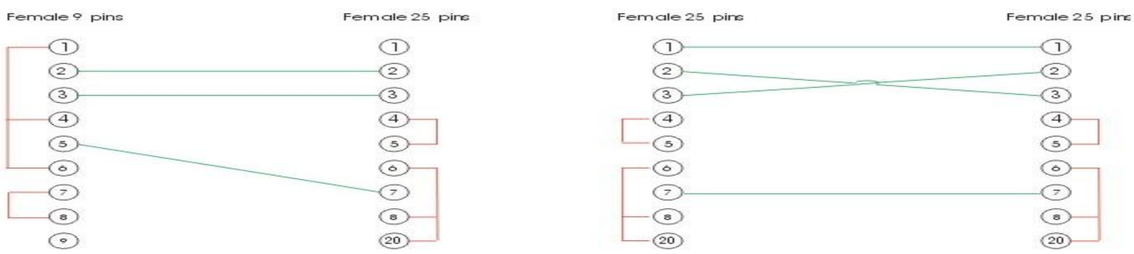


Figura 13.1

The figure 13.1 shows two examples of null-modem cables to link directly the PC (9 or 25 female pins connector) to the diffractometer (25 female pins connector). This cables are rather different to the original, and the diffractometer connector should be in the 25 pins male position 1 of the PW1712 connector (This position is the I/O channel. Position 2 is output only). Remove also the null-modem box which is delivered with the PW1712 (a 12x4x2 cm approximately black box).

To acquire a diffractogram click ***File> Acquire*** or the  button. The order ***File> New*** is executed at the same time. The following 13.2 screen appears:

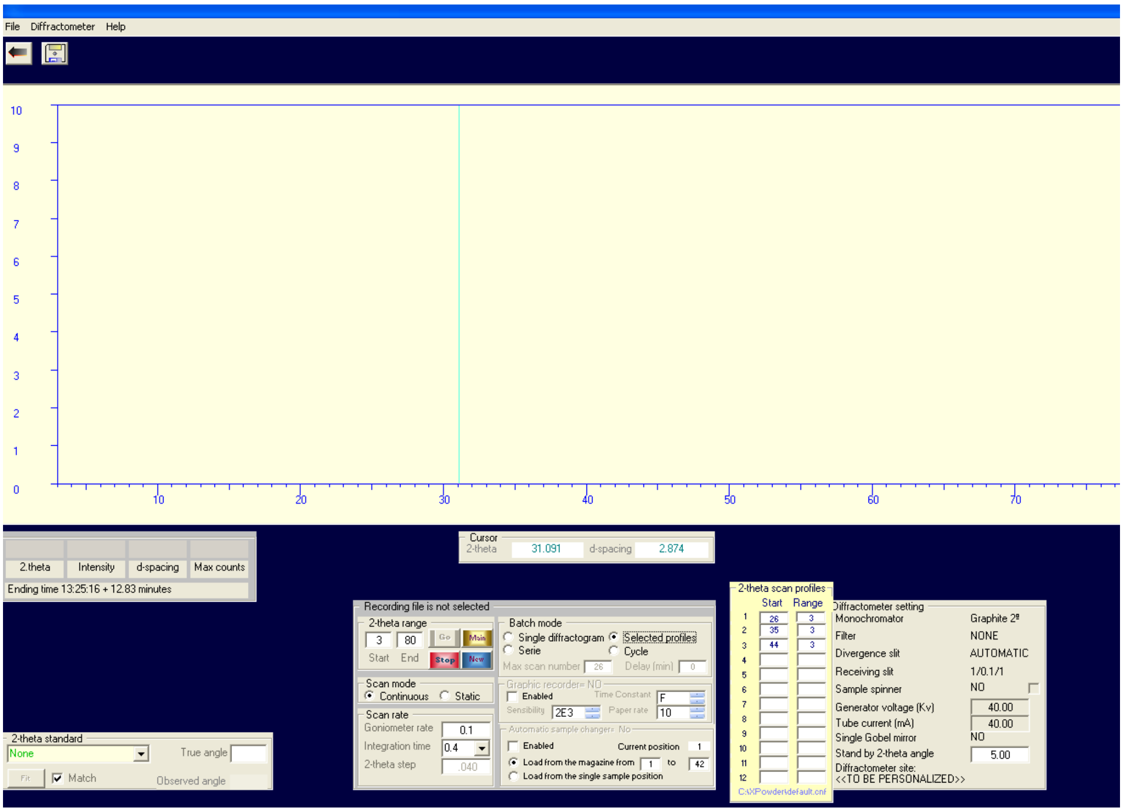
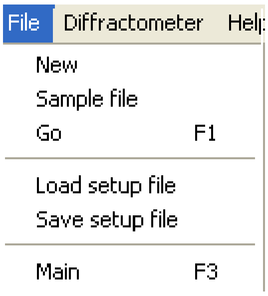


Figura 13.2.

The *File* menu



New. It allows to begin a new data collection from the diffractometer. It is equal to the **New** button.

Sample file. It allows to select a file where the diffractogram will be saved. The format of the data is the same as the one that is shown in the example. It is equivalent to press the button.

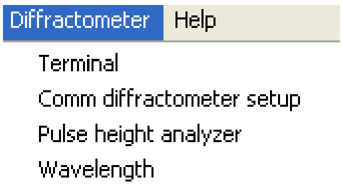
Go. The data collection begins under the conditions that have been set up in the rest of the screen (Start angle, final angle, etc). It is equivalent to the **Go** button.

Load setup file. It loads a configuration file with the **CNF** extension. When accessed to this screen the configuration file loaded by default is **DEFAULT.CNF**. This order is reserved to configure the data collection in agreement with a model (start angle , exploration type, goniometer speed, final angle, etc.) which is used for a certain purpose (identification of mixtures, unit-cell refinement , OA, etc.). These configurations are defined by the user.

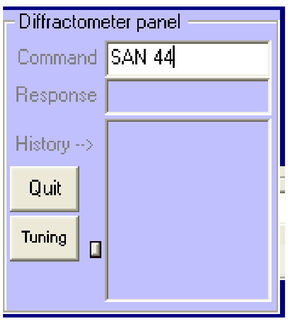
Save setup file. A configuration defined by the user is saved with the CNF extension (it carries out the inverse operation to the previous point).

Main. **XPowder** returns to the main screen. It is equivalent to the or **Main** button.

The *Diffractometer* Menu



Terminal. It shows a small screen to can dialogue with the diffractometer. It is equivalent to the keyboard and screen at the diffractometer control panel, but as remote terminal. The commands are sent by **Command** window and the answers of the diffractometer appear in **Response** window. The **History** window contains the whole conversation. ***Tuning*** button can be used to obtain a graphic of static measures of intensity at the current 2θ angle in instrumental setting processes.



The keyboard ***return*** moves the 2θ angle of the diffractometer to the beginning position. **Response** shows the symbol of the diffractometer system (for example **C =**).

The **Quit** button closes the remote terminal.

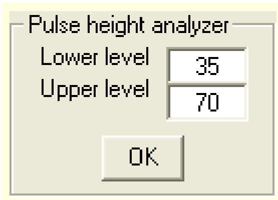
Comm diffractometer setup. It establishes the communication parameters between **XPowder** and the diffractometer. These parameters have to be established in the communication plate of the diffractometer by leaving the microswitches in the appropriate position (see the technical manual of the communication plate) and they should be the same in both the diffractometer and the computer. In case of problems try to modify the parameters of **XPowder** until they match those of the diffractometer. Frequent combinations are:

9600, N, 8,1
4800, N, 8,1
9600, N,7, 2
etc.,

The port of the computer   usually is *Com1* or *Com2*.

Once the communication is established (it can be proved with **Terminal**) save this configuration (***Save setup file***). It can be edited latter with a text editor (***Note Pad*** for example) with the name **DEFAULT.CNF**.

Pulse height analyzer. It establishes the minimum and maximum levels of the pulse height of the discriminator diffractometer counter. These parameters should be adjusted previously in the diffractometer (consult the technical manual).



Wavelength. It allows to selecting the wavelength or the X-ray tube installed in the diffractometer.

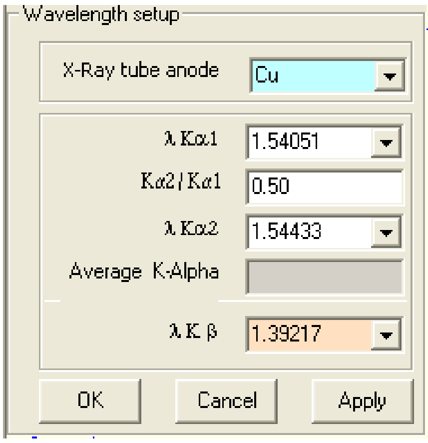
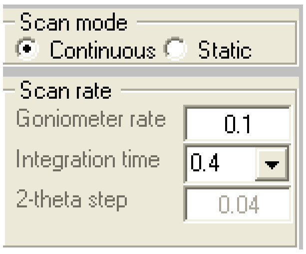


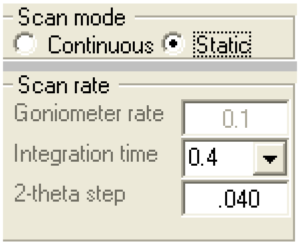
Figura 13.3

Setting the experimental conditions

Recording mode

There are two modes of data collection. The first one moves the 2θ angle of the diffractometer at continuous speed and the counts are accumulated by the counter at certain intervals (***integration mode***).





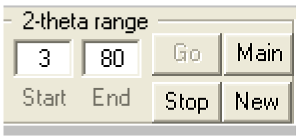
The second mode consists of measuring statically during a certain time in a fixed 2θ angle while the counts are accumulated. This operation is repeated at the next 2θ angle and so on until arriving to the final 2θ angle (***static mode***). Naturally both recorded modes are carried out in automatic mode.

The first one produces softened profiles, but also a small deformation and stretching in the peaks. The second one is more accurate and it doesn't deform the profiles, but it produces more random noise.

The first mode can be improved by diminishing the exploration speed. The second mode can be improved by increasing the integration time.

To select the ***integration mode***, press the ***Continuous*** option button. To select the ***static mode*** press the ***Static*** button. ***Goniometer rate*** box marks the angular speed of the goniometer. ***Integration time*** box marks the time during which the counter accumulates counts and ***2-theta step*** box marks the increment of 2θ angle between two successive measurements. Only the boxes that can be modified are actives.

Exploration interval. The initial 2θ angle is entered in the ***Start*** box and the final 2θ angle in the ***End*** box. The starting time and the recording time appear in the text box:



Diffractogram capture. Press the ***Go*** button when the experimental conditions have been set up. The diffractogram capture can be stopped at any moment (***Stop*** button). A continuous re-scale of the intensities axis as a function of the maximum of counts is done during the data collection.

Data format. The diffractogram data are codified in ASCII text. The experimental conditions are set up in the first fifty lines. The first line is a heading with free format, consist of a key word(s) (*Step size* = for example) and an argument (0.040 in this same example). Empty lines can be numbered to identify their position (line 41 for example) and the line 50 is "*Data"* to indicate that next lines corresponds to experimental measurements. Data are written in two columns separated by one or more spaces. This format guarantees that the data can be interpreted by any user and read or imported by any program in any operating system. Lines begin with *Line* keyword are ignored.

Example:

```
XPowder diffraction software. PLV file format Ver. 3.0
Sample= AFRICA.PLV
Site= Universidad de Granada (Spain)
User= Crista-Mine-Gr
Date= 28/10/2003
Time= 13:06:15
Start 2-theta scan= 10.000
End 2-theta scan= 80.000
Step size= 0.040
Scan mode= Continuos
Integration time(sec)= 0.4
Anode= Cu
Filter= NO
Monochromator= Graphite 2Ý
K-Alpha 1=  1.54051
K-Alpha 2=  1.54433
Ka2/Ka1 Ratio=  0.5
K-Beta=  1.39217
Automatic sampler changer= NO
Single Gobel mirror= NO
Divergence slit= AUTOMATIC
Receiving slit= 1/0.1/1
Generator voltage(Kv)= 40.00
Tube currrent(mA)= 40.00
Maximun counts=  10
Line   26
Line   27
Line   28
Line   29
Line   30
Line   31
Line   32
Line   33
Line   34
Line   35
Line   36
Line   37
Line   38
Line   39
Line   40
Line   41
Line   42
Line   43
Line   44
Line   45
Line   46
Line   47
Line   48
Line   49
Data
 10.000        4
 10.040        5
 10.080       10
 10.120        8
 10.160        7
 10.200        5
 10.240       10
 10.280        9
 10.320       10
 10.360       11
 10.400        6
 10.440       11
 10.480        7
 10.520        6
 10.560        9

    ...            ...
    ...            ...
    ...            ...
```

Setting the 2θ angle zero mark. It can be carried out automatically by recording the diffractogram of a well-known standard (for example, silicon) or with an internal standard. **XPowder** allows to use the list of the ***std.txt*** file for this purpose. The following procedure should be performed:.

1. Select the standard from the list as shown in the image.

2. Record the diffractogram.

3. With the left button click on the symmetry line (or on the maximum) of a well-known pick from the diffractogram.

4. With the *Alt* + left mouse button click near the position of the standard line to which the maximum must be adjusted. The true 2θ angle can be input manually in the ***True angle*** box. If this is the case step 1 it is not necessary.

5. Press the ***Fit*** button and then the diffractometer corrects the zero offset automatically.

To observe the quality of the adjustment, mark the ***Match*** check box before pressing ***Fit***. Then, the diffractometer measures automatically the standard again.

Recording strategy. When selecting the ***Single diffractogram*** option button, the files of each recording should be named one by one. Whit this option, a file name should be selected before recording each run in order to save the recorded data Figure 13.4.

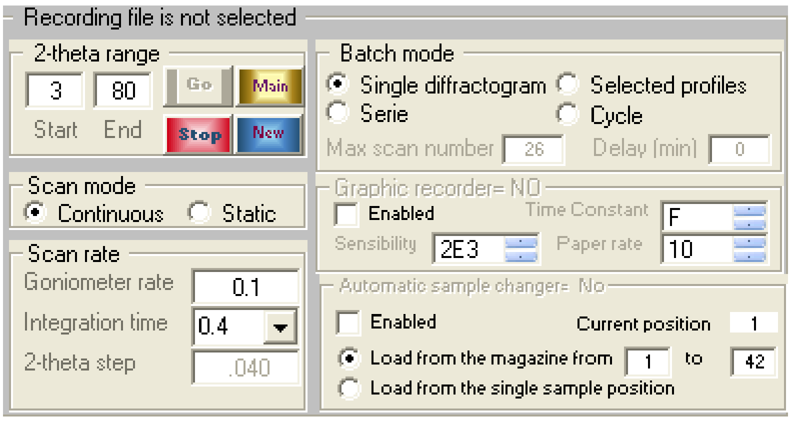


Figura 13.4

f the option ***Serie*** is selected, the samples are named by adding an order number to the original file name. For example, if the name is ***example*** the program will output the files ***example_001.plv***, ***example_002.plv***, etc. It is necessary to press ***Go*** between successive diffractograms.

If the ***Cycle*** option is selected, the number of recordings selected in the box ***Max scan number*** will be carried out automatically (10 in the example) with the *time delay* input in the ***Delay (minutes)*** box (30 minutes in the example). The name of each file follows the same rules as in ***Serie***. This mode is used to study changes of phases, hydration grade, crystallinity, etc. It is also used coupled to changes in temperature. The maximum number of diffractograms is 999 and the delay time betweendiagrams can be set to zero (without wait) or as long as desired (always in minutes).

If Selected profiles is checked, we can select individual reflections in order to be secuencially scanned (figure 13.2, 2-theta scan profiles).

It can be selected also:

- Automatic sample changer: Include in 'Default.cnf' the line

```
AutomaticSamplerChanger = PW 1775
```
or
```
AutomaticSamplerChanger = PW 1775
```

- Spinner: Include in 'Default.cnf' the line

```
Spinner= PW 1774
```
or
```
Spinner PW 1774
```

- Graphic recorder: Include in 'Default.cnf' the line:

```
GraphicRecorder = PW 8203A
```
or
```
GraphicRecorder = PW 8203O
```

Home

Updates

Version 2004.04.49. (11-05th-2008)

1. Starting with this release of the program , the searching do not necessarily uses the full diffractogram, as explained in Chapter 2, but is restricted to the selected 2θ interval. This allows you to search unique reflections on isolated so comfortable.

For example, a residual reflection, which on a previous search has not been assigned to any component, can be selected to complete the list of identified phased. The modification of the program is useful in samples with minority components or or poor crystallization.

2. It has removed the check box Force subtraction in the tool 'Matching', Chapter 5, which now stays as in Figure A.1.

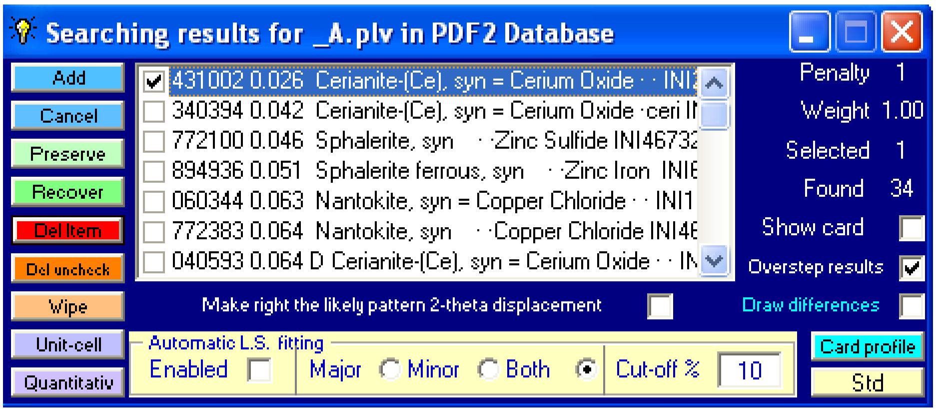


Figure A.1.

Now, the subtraction component option appears as in Figure A.2, after it has calculated the pattern record with the order Card profile .

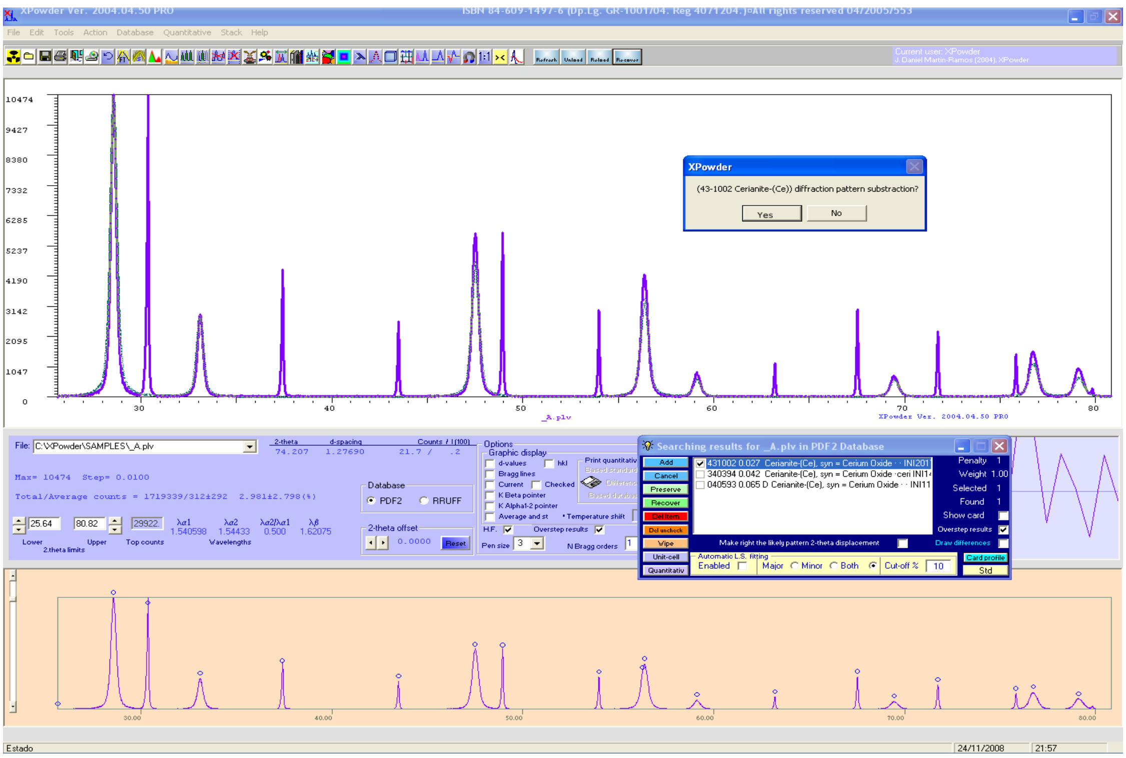


Figure A.2

Version 2004.04.50. (11-10th-2008).

File extensions' .asc 'and' .xy ', in addition to the classic ".txt" for text file formats (XY), which already existed in the early versions of XPowder, have been included again.

Versions 2004.04.53. (01-08th-2009) and 2004.04.54 (01-14th-2009)

Many researchers record their diffractograms in limited angular intervals (eg explore 2θ between 5º and 45º). It is common for example in studies of the clay minerals or when used portable diffractometers without mobile components. However databases (PDF and AMSCD) contain information on crystalline phases patterns registered outside the limits explored in laboratories. Thus, some recods contain only d-spacing greatest 3.00 Angstroms while others (especially the most modern) contain information that goes lesser to 0.7 Angstroms.

In order to optimize the search conditions of crystalline phases, users can now instruct the program so that unused 2θ zones are excluded from the databases. This can be done at the time of the option to install Database Install or Update XPowder in XPowder homepage. The searchings are made with much greater speed and safety because only the ranges of records that best matching in the respective laboratories are used for adjustments.

The values for angle interval of database can be entered in boxes Higher d-spacing and Lower d-spacing in Figure A-3.

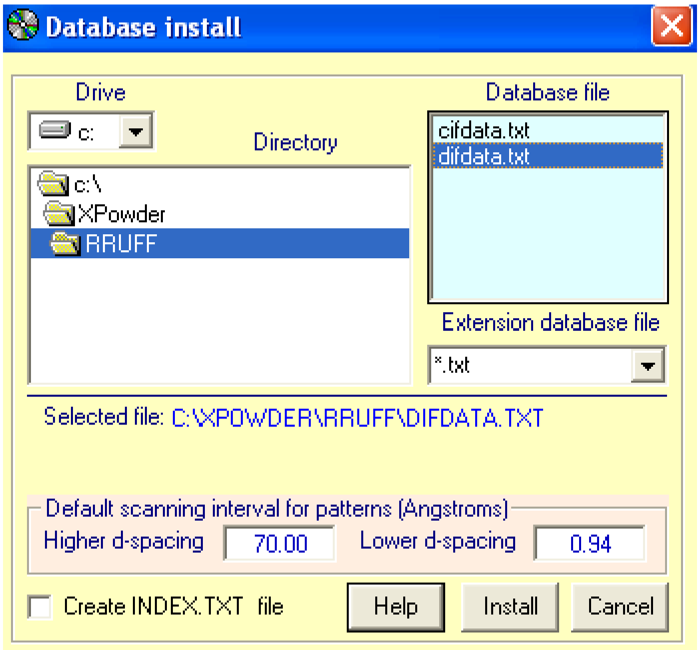


Figure A-3. The program will exclude d-spacing lesser than 0.94 Angstroms and greater than 70 Angstroms during the installation of the database AMSCD.

Angular areas excluded from the database appear in the framework Database and are drawn with a gray background in Advance searching tool (Figure A-4).

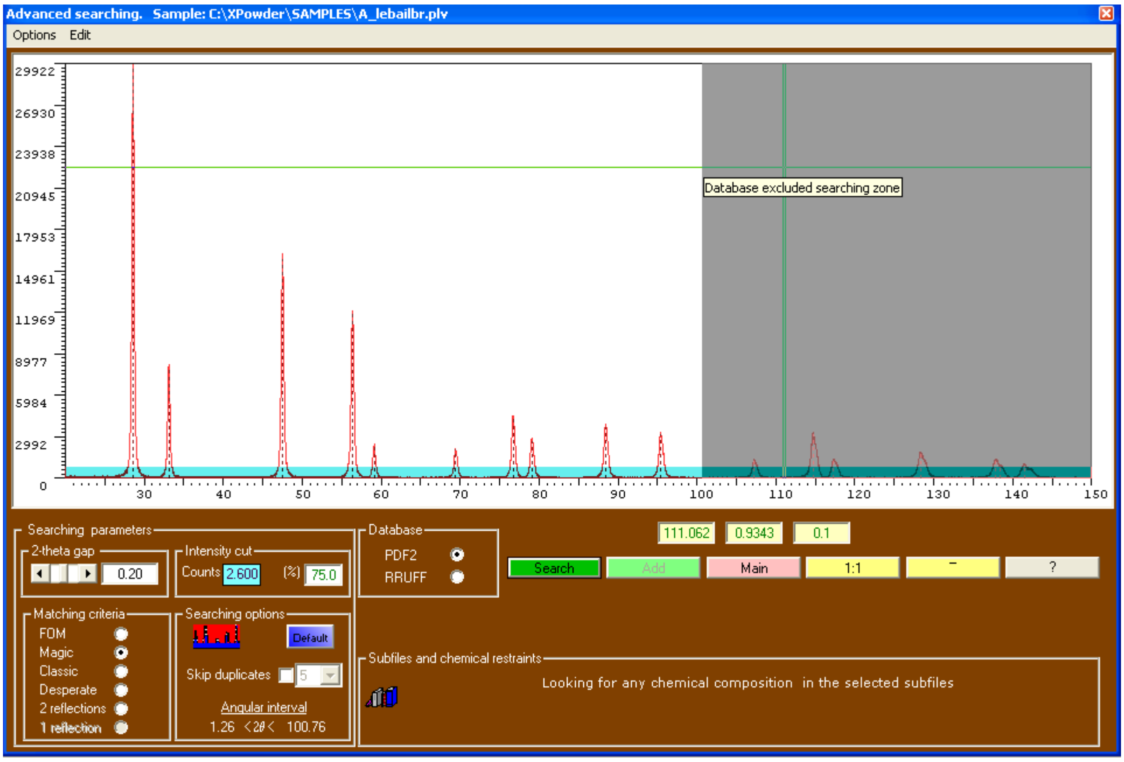


Figure A-4. During the searching, the program does not take into account the d-spacing of the database for higher values of 2θ = 110.06 ° (grey zone). In general, this area is not used for identification of crystalline phases. To use it, would have to reinstall the database with value 'Lower d-spacing' of 0797 Angstroms, which corresponds to approximately 150 ° for radiation $CuK_{\alpha 1}$.

Since version 2004.04.54 has been including in Matching criteria frame, a new approach 2 reflections that uses only two of the diffractogram reflections to matching with the high intensity reflections of database records. When this option is used, the number of possible solutions is high in general, due to the lack of information used in the calculations. It is therefore appropriate to provide supplementary information to the program (about chemical composition, for example ). This approach should be used in diffractograms having small scanning intervals (eg 2 <2θ° <50, or to identify minority phases. Also, from version 2004.04.54, the second searching options of 'Desperate' has been renamed to '1 reflection' , because it uses in searching only one reflection.

To find the database records that match a single reflection of experimental pattern, this reflection should be exclusively selected by the zoom and then click Search or Add . The searching option '1 reflection' will be changed by the program itself and then it carries out the automatic searching.

Version 2004.04.57. (02 - 11th -2009)

1. The new tool Matching is more powerful (Chapter 5).

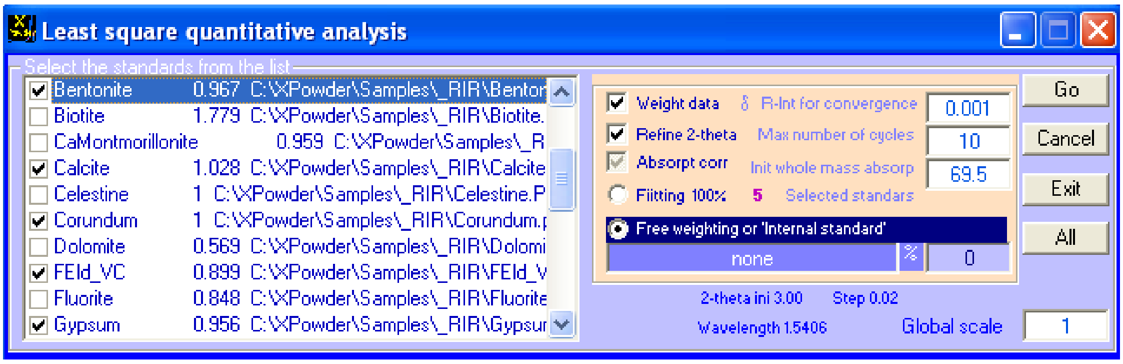
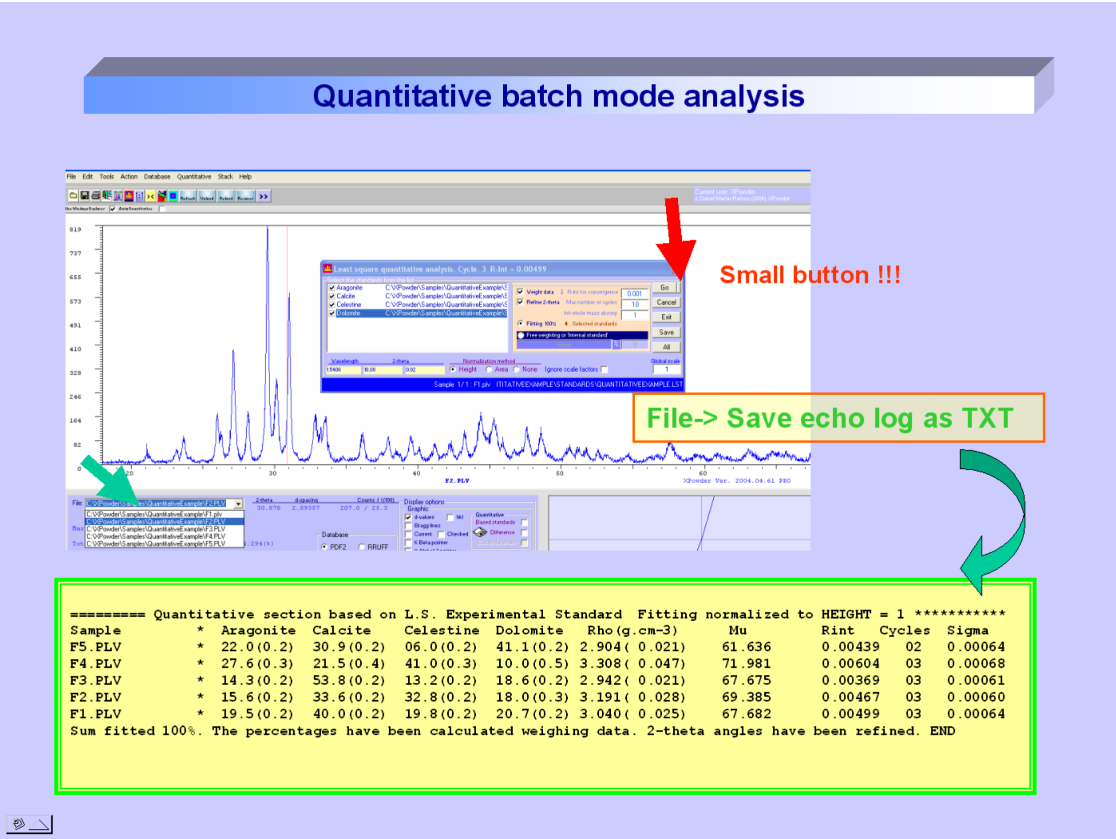


Figure A.5. This tool replaces the one described in A.1

2. More choices and better options for quantitative analysis with experimental standards (Chapter 7 and PTT)

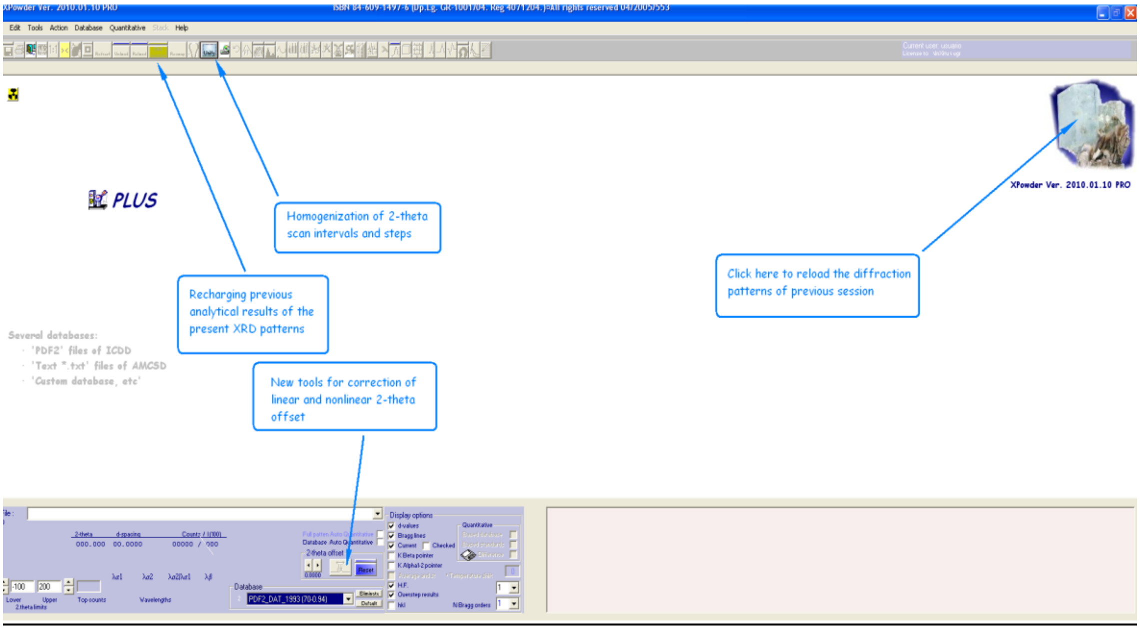


3. Three new data formats are recognized directly by XPowder:

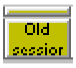
- The ascii dataformat '*.X_Y' of the diffractogram file output of PowderCell programs of W. Kraus & G. Nolze (2000). *Federal Institute for Materials Research and Testing. Rudower Chaussee 5, 12489 Berlin, German)* .
- Sietronic '*.cpi' format.
- '*.nja' de Seifer.

Index

XPowder 2010.01.10. New features. (May, 2th 2011)



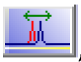
1. Reloading of previous session patterns.  Clicking on the picture of the mineral (beryl) of the home screen, reloads all diffractograms of the last working session, but calculations are excluded (searching-match, quantitative, etc.) .

2. Reloading of previous analytical results… 

Retrieves the previous analysis (historic) carried out on those XRD patterns that are currently in XPowder memory (searching-match, quantitative, etc.). Like other parts of this program, the large button retrieves data from the active sample, while the top bar performs the same action on all loaded XRD patterns.

3. Homogenization of 2θ scan intervals and steps. 

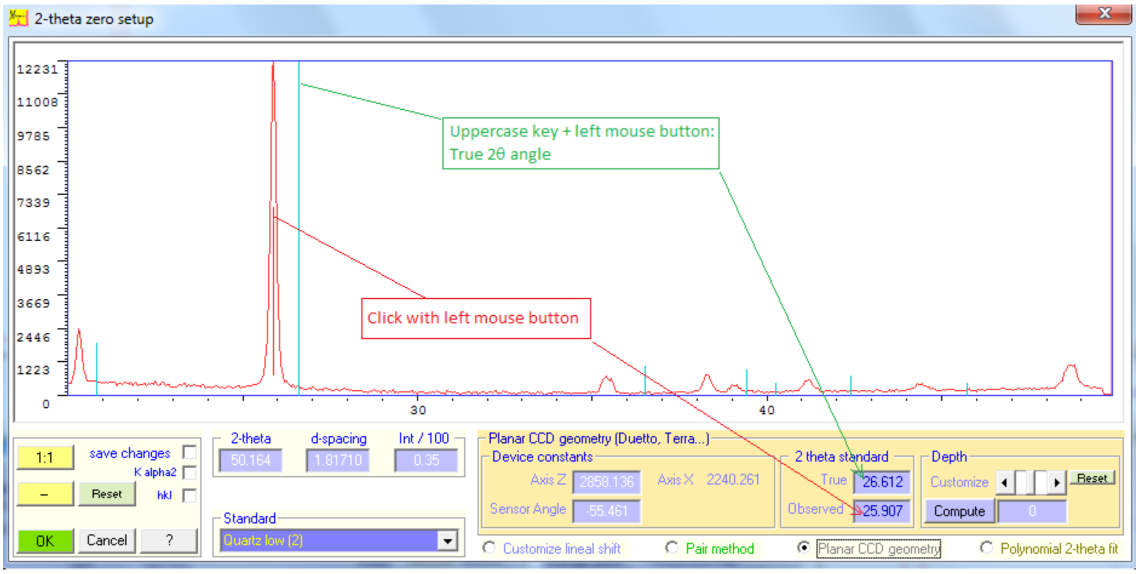
Standardizes 2θ angles (initial, final and steps) for all those XRD patterns loaded. This action is performed even if the initial data formats are quite different. The order is also available in **2D** and **3D** stacking windows. The range is homogenized using the higher initial 2θ values, the smaller final 2θ values and the minor 2θ interval. When some diffractogramme has the scan step variable, data are converted into constant step (histograms). Occasionally, when the initial data are too heterogeneous, this command may need to be run twice.

4. Linear and nonlinear 2θ zero shift. By clicking button , four options are availables:

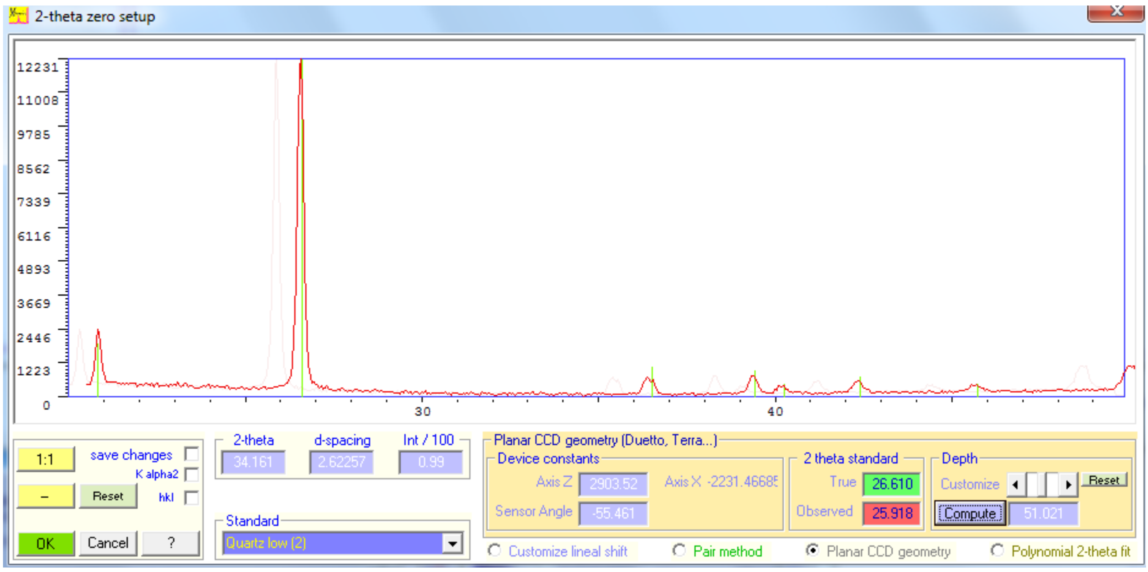
- 4.1. Customize lineal shift (See Chapter 3)
- 4.2. Pair method (See Chapter 3)
- 4.3. Planar CCD geometry
- 4.4. Polynomial 2θ fit

- 4.3. Planar CCD geometry: This nonlinear correction is used with flat detector diffractometers where the sample position can not be fitted accurately. Requires knowing the approximate distance between the sensor and the sample, and the angle between sensor and X-ray beam. Can be used either one reflection standard (True and Observed boxes and Compute) or the Customize cursor to move the diffractogram to the correct position

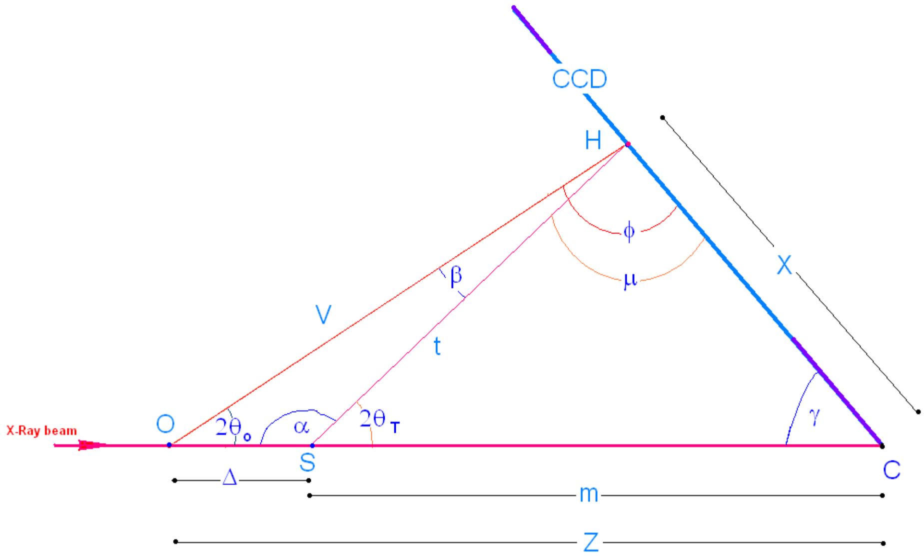
Prior to correction:



After correction:



Planar CCD geometry correction details:



O = Diffractometer centre (ideal sample position)
S= real sample position
γ = 90º - Sensorangle
Z= Axis Z length. Distance between O and CCD along primary X-Ray beam
X = Coordinate along Axis X
Δ = Displacement of diffractometer center ("Depth")
$2\theta_o$ = Observed (measured) 2θ
$2\theta_T$ = True 2θ .

2θ correction in function of 'depth' X-Ray penetration (= sample offset along primary X-Ray direction)
Δ is a know or estimated data
In **OHC** triangle, by using sine theorem:
$\mathrm{Sin}2\theta_o / X = \mathrm{Sin}\,\gamma / V = \sin\phi / Z$ $\qquad \gamma = 90^o$ - Sensorangle
$V = X \cdot \mathrm{Sin}\,\gamma / \mathrm{Sin}2\theta_o$ [1]
$X = Z \cdot \mathrm{Sin}2\theta_o / \sin\phi$ $\qquad \phi = \pi - \gamma - 2\theta_o$
$X = Z \cdot \mathrm{Sin}2\theta_o / \sin(\pi - \gamma - 2\theta_o)$ [2]
In **OHS** triangle, by cosine theorem:
$t^2 = \Delta^2 + V^2 - 2\,\Delta\,V \cdot \cos 2\theta_o$ [3]
And by sine theorem :
$\mathrm{Sin}\,\alpha / V = \mathrm{Sin}2\theta_o / t$ $\qquad \mathrm{Sin}\,\alpha = \mathrm{Sin}(\pi - 2\theta_T) = \mathrm{Sin}2\theta_T$
$\mathbf{Sin2\theta_T = V/t \cdot Sin2\theta_o}$ [4]
By replacing V [1] and t [3] in [4]

$\mathrm{Sin}2\theta_T = (X \cdot \mathrm{Sin}\,\gamma) \;/\; (\Delta^2 + V^2 - 2\,\Delta\,V \cdot \cos 2\theta_o)^{½}$
Where V and X are calculated by [1 and [2]
Δ is the sample offset along primary X-Ray beam direction in equal units of axis Z.

This formula let to correct the deformation of 2θ scale of any diffractogram obtained from CCD. Δ can be estimated from a reflection standard (see next page) or by a cursor changing Δ value while the new diffraction pattern is matched.

Calculation of 'depth' X-Ray penetration (= sample offset along primary X-Ray direction) from a standard reflection

$2\theta_T$ - $2\theta_o$ are know data

In **OHS** triangle, by sine theorem:

$\mathrm{Sin}\,\alpha / V = \mathrm{Sin}2\theta_o / t = \mathrm{Sin}\,\beta / \Delta$ [6]
$\beta = \pi - \alpha - 2\theta_o = \pi - (\pi - 2\theta_T) - 2\theta_o = 2\theta_T - 2\theta_o$

On the other hand:

$\mathrm{Sin}\,\alpha = \mathrm{Sin}2\theta_T$

[6] can be rewrited:

$\mathrm{Sin}\,2\theta_T / V = \mathrm{Sin}2\theta_o / t = \mathrm{Sin}\,(2\theta_T - 2\theta_o) / \Delta$

Turn out Δ:

$\mathbf{\Delta = [V \cdot Sin\,(2\theta_T - 2\theta_o)\,] / Sin\,2\theta_T}$ **[7]**

Where:

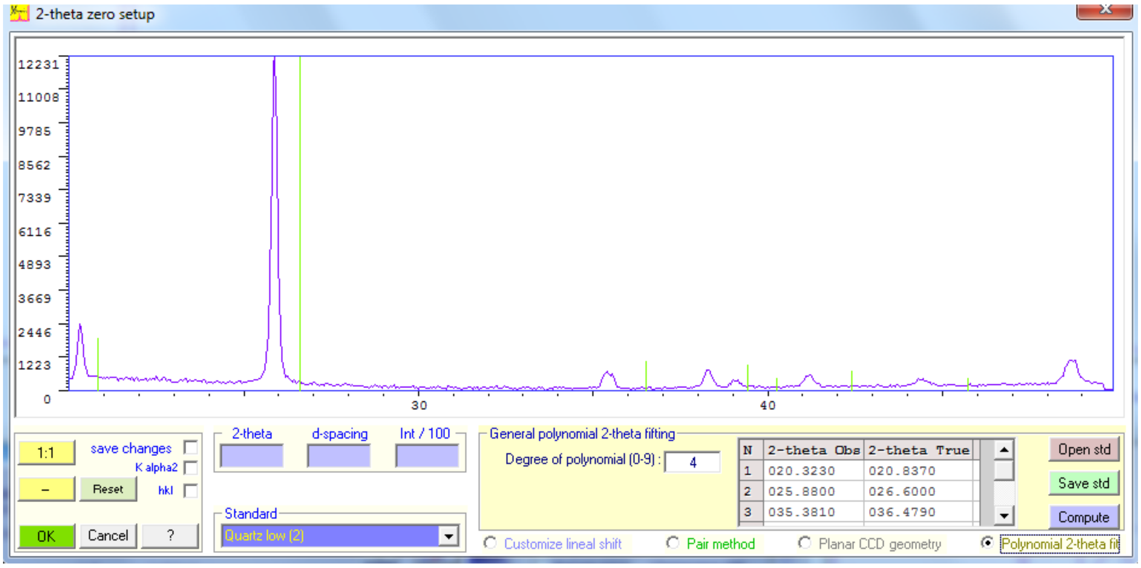
$V = X \cdot \sin\gamma / \mathrm{Sin}2\theta_o$ [1]
$X = Z \cdot \mathrm{Sin}2\theta_o / \sin(\pi - \gamma - 2\theta_o)$ [2]
$\gamma = (90^o - \mathrm{SensorAngle}^o)$
Z = axisZ (distance from ideal simple position to CCD along X-Ray beam direction)

Then:

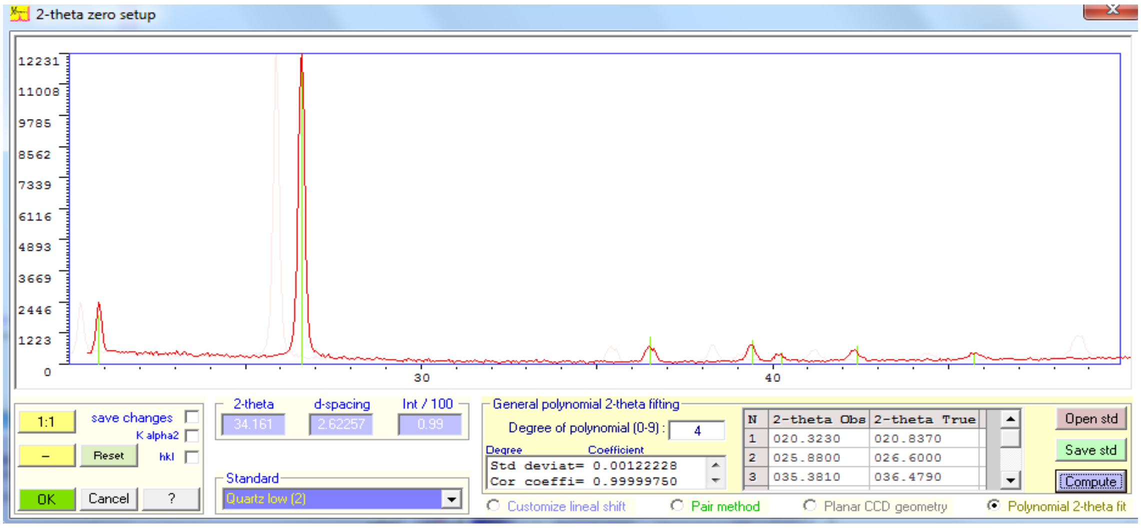
$$\boxed{\Delta = [Z \cdot \mathrm{Sin}\,\gamma \cdot \mathrm{Sin}\,(2\theta_T - 2\theta_o)] \;/\; [\,\mathrm{Sin}\,(\pi - 2\theta_O - \gamma) \cdot \mathrm{Sin}\,2\theta_T\,]}$$

- 4.4. Polynomial 2θ fit. This algorithm has general character and allows any non-linear adjustment of the angle by using a standard sample and a polynomial of degree up to 9 maximum. This method can be used instead of 4.3, but requires an examination of reflections of the entire 2θ angular scanned range.

Prior to correction:



After correction:

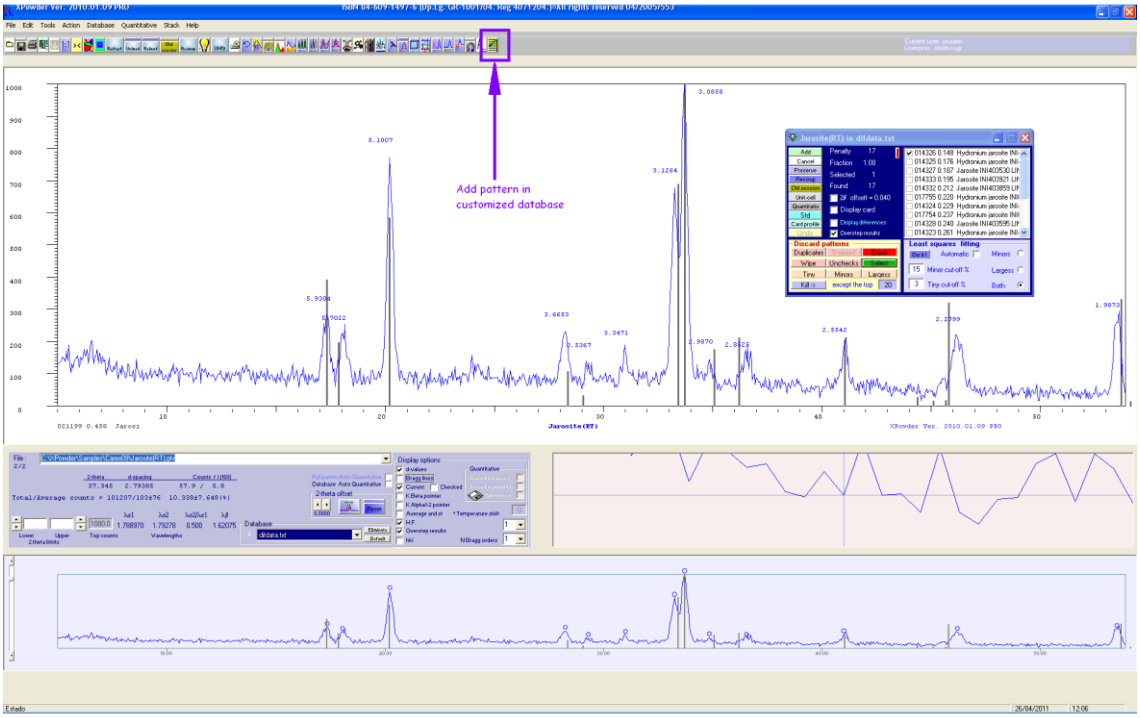


The observed and expected data they can direct entry into the table, or can be placed in an archive with '.T_O' extension, created with a text editor (use Open std and Save std):

Example of 'T_O' archive:

Head (any)
20.323 20.800
25.880 26.600
35.415 36.510
38.331 39.390
39.120 39.420
41.178 42.410
44.334 45.700

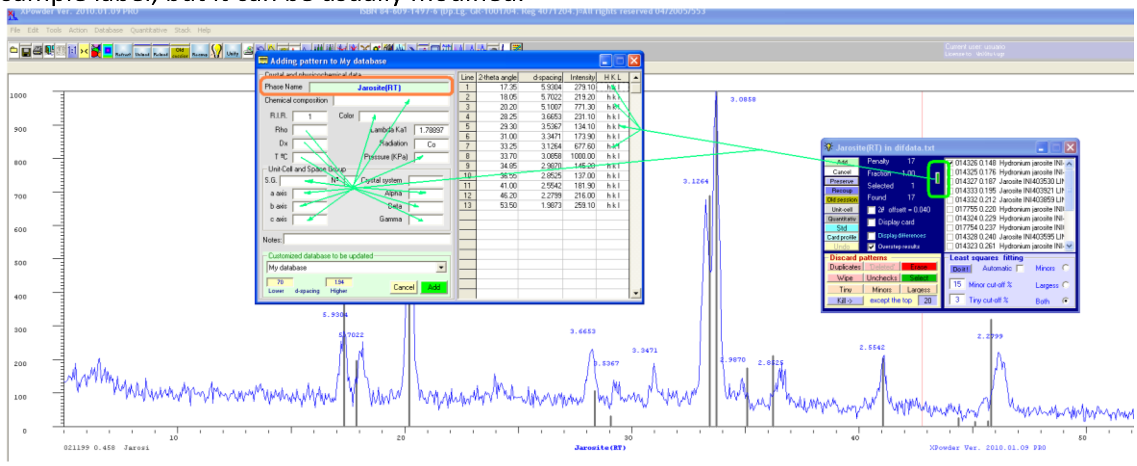
5. Customized databases. An unrestricted number of custom databases can be used. The generated files have the extension MYD and they can be installed at any time on various computers, just like any other database. The procedure to build and to maintain a custom database is:



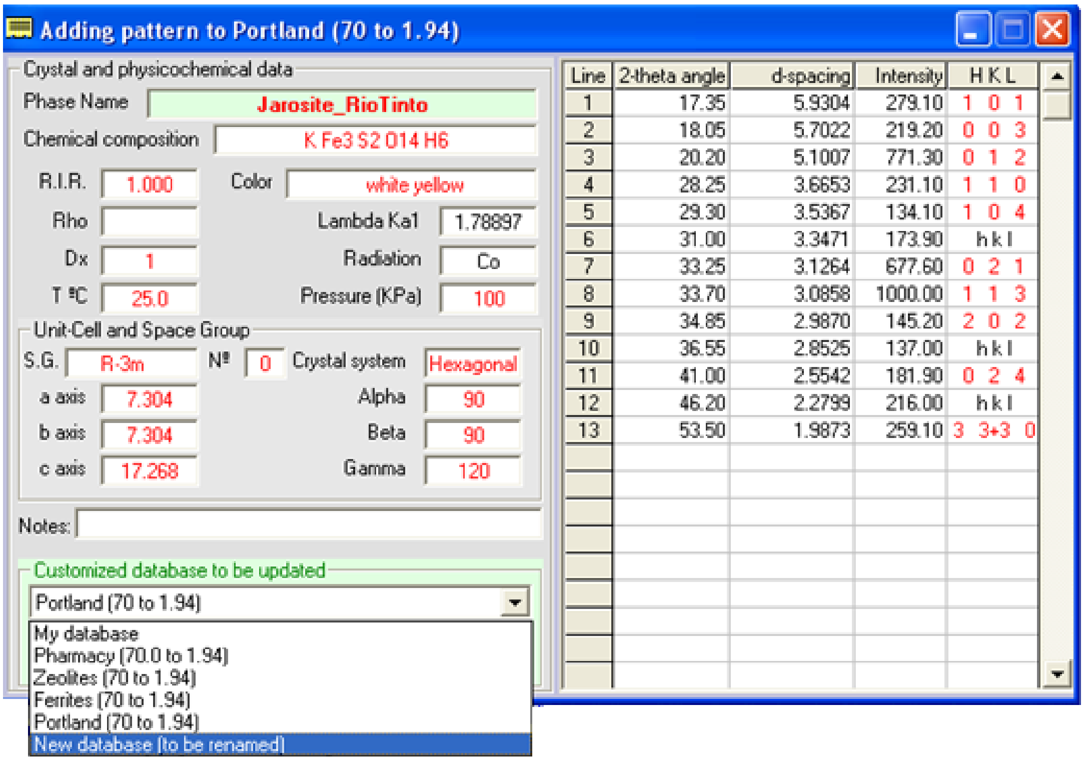
5.1. Load an experimental pattern and optionally make the identification of the crystalline phases.

5.2. Click button of the tool 'Results' in order to add the current card from an existing database to a custom database.

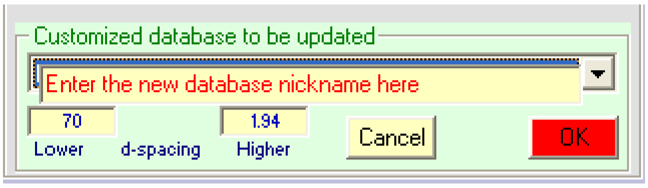
5.3. Alternately, select the reflections of crystalline phase of experimental diffractogram by clicking on pattern reflections. Then, push on button of main menu to add the experimental current Bragg's reflections as further card into an existing database. Optionally, you can export crystallographic data (unit-cell, hkl, etc) from previous database () or write directly into text boxes. The default phase name is the sample label, but it can be usually modified.

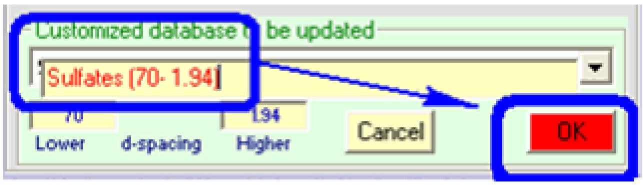


5.4. Select the destination customized database (a preexisting or a starting custom database).

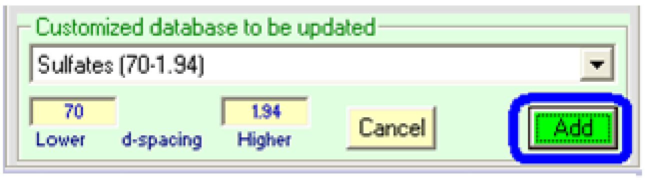


5.5. If a new database is selected, rename it and push OK button:





5.6. Add the new card (**Jarosite_Rio Tinto** in the example) to the custom database (Sulfates [70-1.94] in the example).



Note: The index files of each database are placed in the directories:

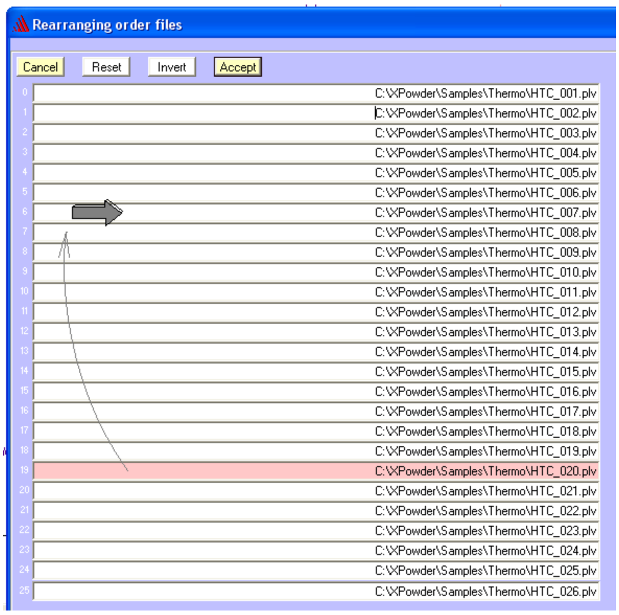
Program Directory\ DBlog\DB_x

Where x are sequential integers for all databases . The value x=0 is reserved to the starting '*MyDatabase.myd*'.

6. Rearranging diffraction patterns

This tool is very helpful to change the relative position of the diffractograms in 2D or 3D clusters.

- On the ‘Home screen’ push the right button in the mousse and select ‘Files/Sorting patterns’.
- On the ‘Stacking screen’ push the right button in the mousse and select “Sorting files’.



Drag the file with the left mouse button to the new position.

Home

XPowder12

New features.

Ver 2012.02.01. General index

- Powerful Kβ stripping function.
- Import additional diffractogram formats, including the direct conversion of *Chemin* diffractometer images of *Curiosity* Mars Rover of the *MSL* project to (x,y) text files.
- File reports in *Adobe pdf* format.
- Ability to save and restore complete work sessions.
- Display of partial components in full-profile quantitative analysis.
- A new tool allows continuous zooming into diffractograms, both laterally and vertically.
- The databases installed previously with the old program **XPowder** can be used directly.
- Search-match, quantitative analysis, 2θ correction and profile tool are more compact than in the old **XPowder** program.
- In quantitative analysis with **XPowder12** program, the acronym ***PIR*** *(Pattern Intensity Ratio)* is used instead of the old ***RIR*** (*Reference Intensity Ratio*), because this term is usually calculated from a single reflection (the highest value in each phase divided by the highest value of a standard, i.e. corundum). However, both programs use the concept ***PIR***, which is far more accurate.
- The window program size can be easly scaled.
- A new fast method for full-profile quantitative analysis of components using 'Dirac' patterns, convolution and PIR scale factors.
- XPowder12 give access to the free database P2D2 (Predicted Powder Diffraction Database). XPowder12 compiles directly this database, when text raw files are installed.
- Additional background subtraction method.
- Area under selected zone.
- Bruker RAW patterns
- Critical Update. Database Color Patterns
- Excluding elements from the periodic table in search-match.
- Version 2004.04.35

XPowder and **XPowder12** can be used simultaneously. In this case it is preferable to install the programs in two different folders.

XPowder12 home screen

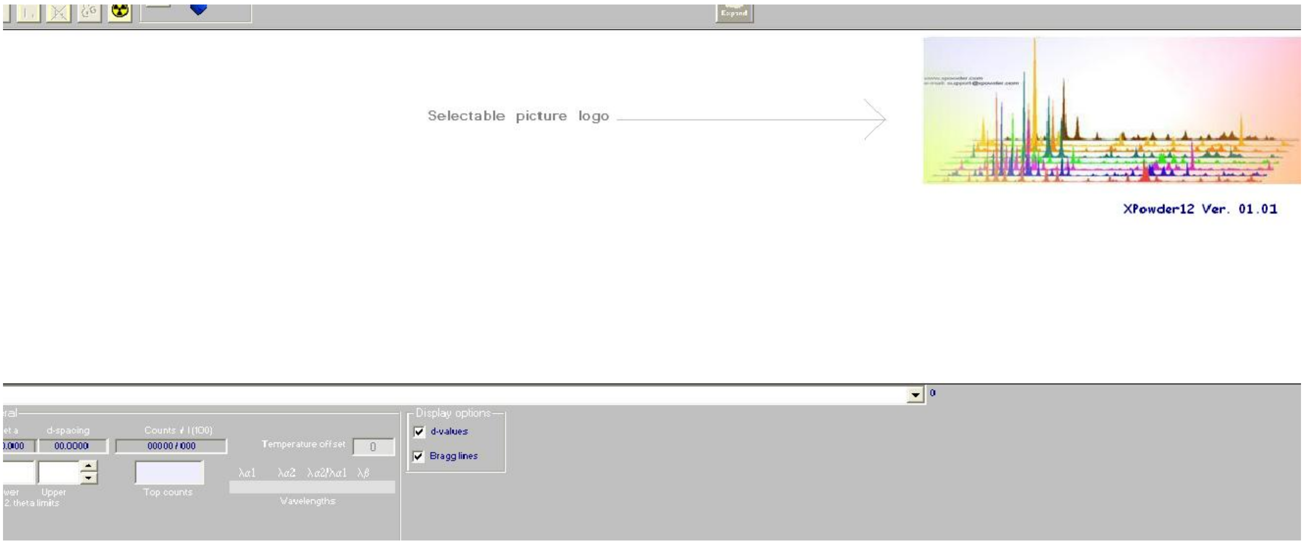


Figure 12.1. Home screen of **XPowder12**. The picture logo can be modified by including a line of the type 'Logo = Path_picture' in the 'Xpowder12.ini' file. Alternatively, the logo picture file named 'Logo.jpg' in the folder XPowder12 program can be replaced by any other picture.

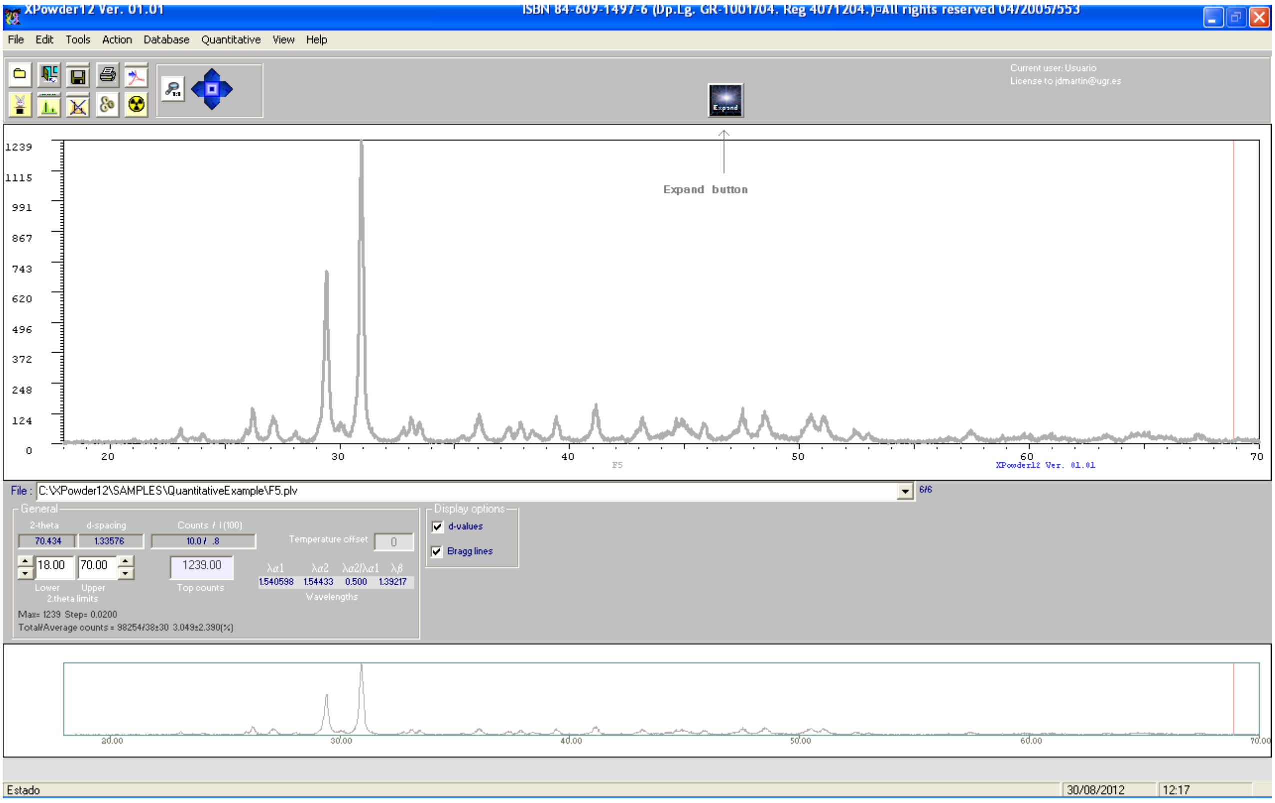


Figure 12.2. Up to fifty XRD patterns can be loaded simultaneously using the 'File' menu. In the figure the basic functions are shown. Sophisticated data analysis tools appear when clicking the button 'Expand'.

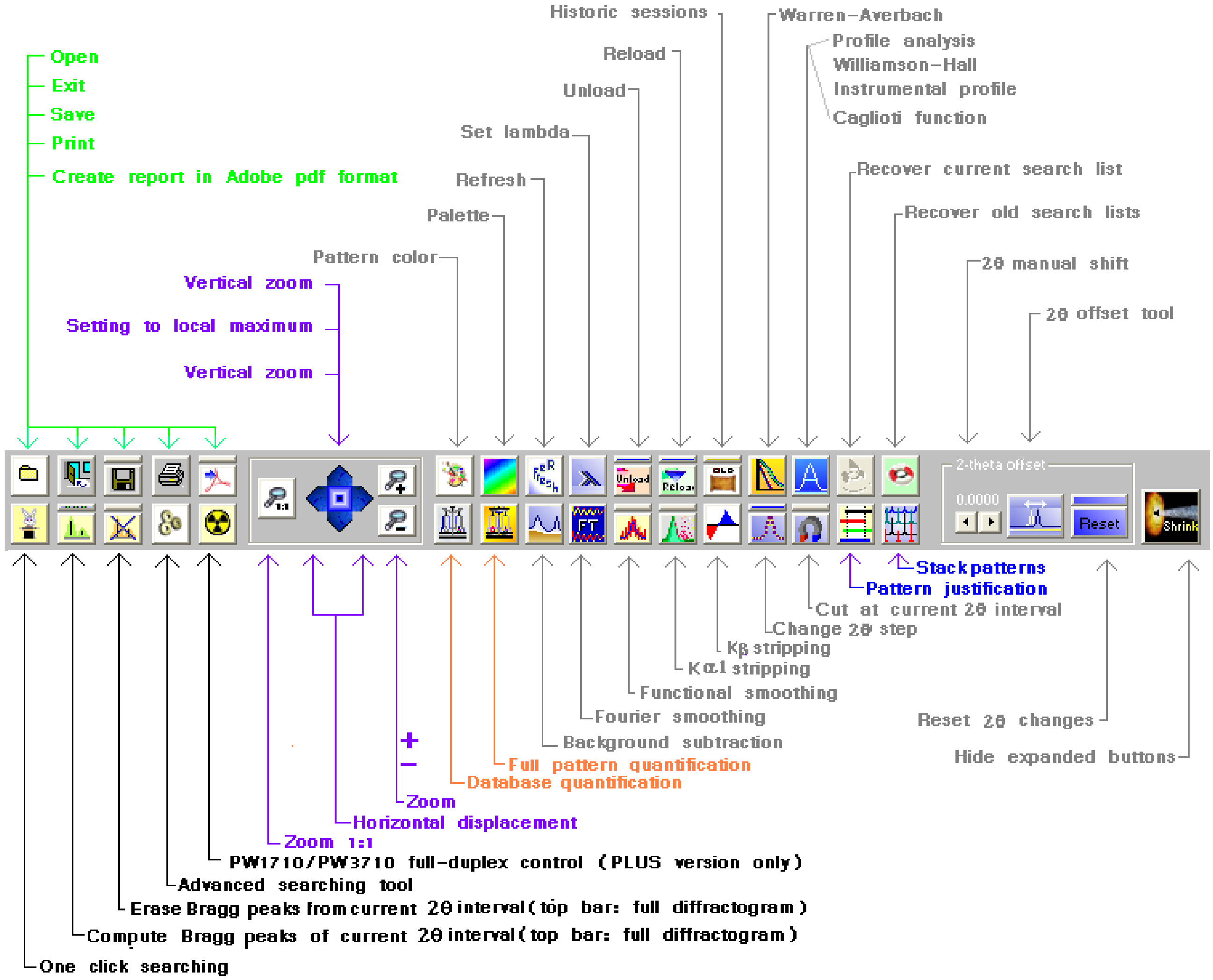


Figure 12.3. Main commands in the expanded 'Main menu' of **XPowder12** program.

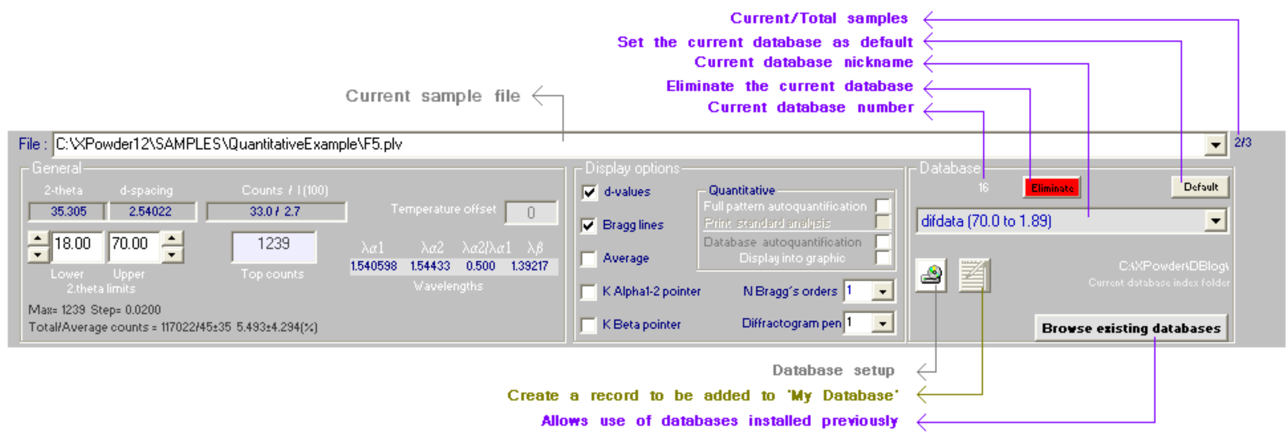


Figure 12.4. Dialog box for modifying diffractogram display settings and selection of the database to be used by data analysis tools.

SEARH and MATCH

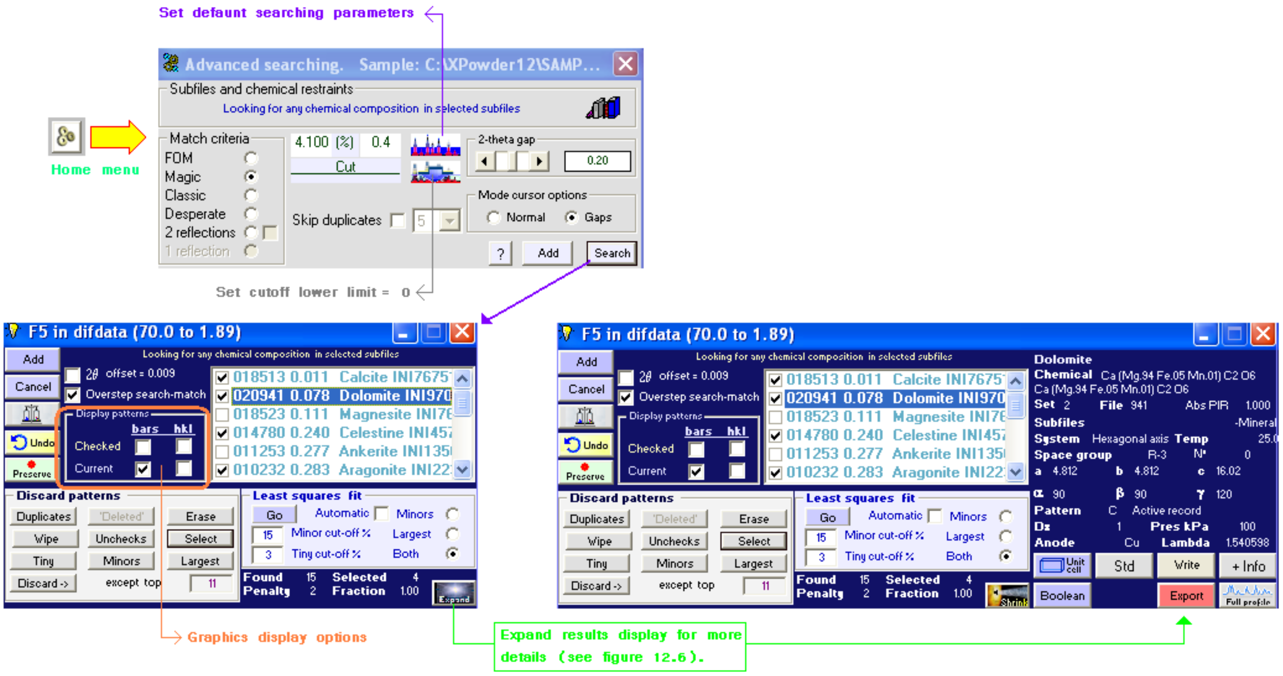


Figure 12.5. Advanced searching tool (above) and basic results display below).

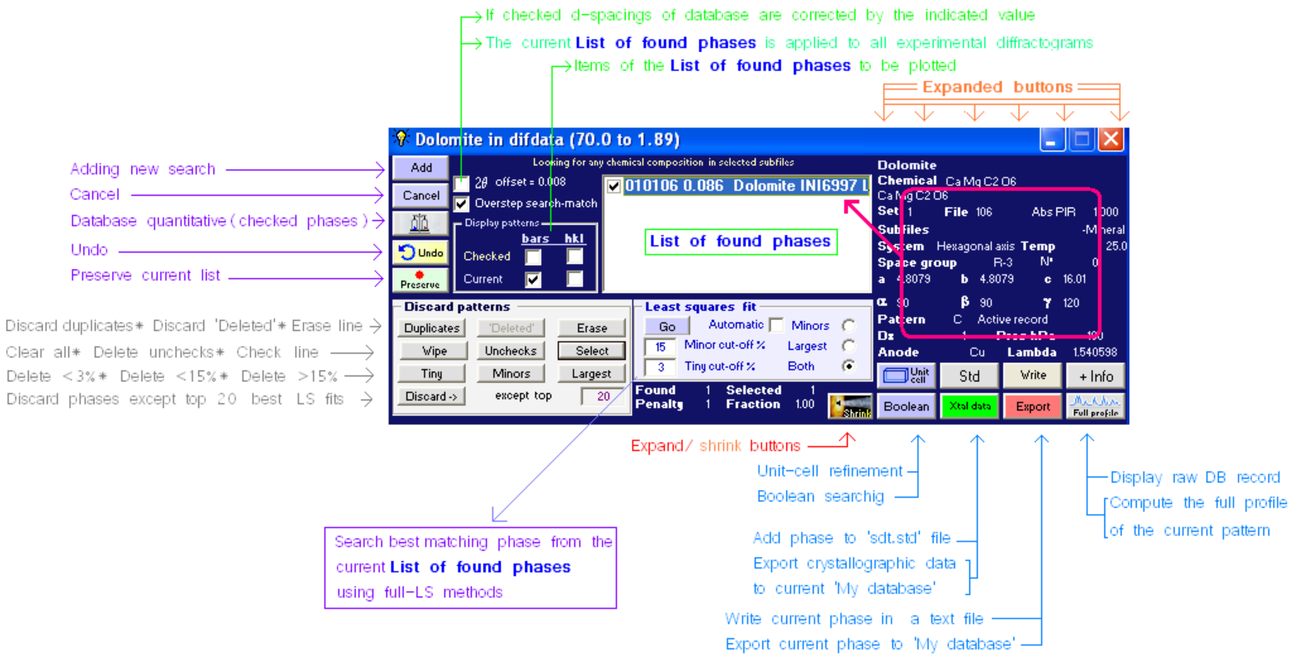
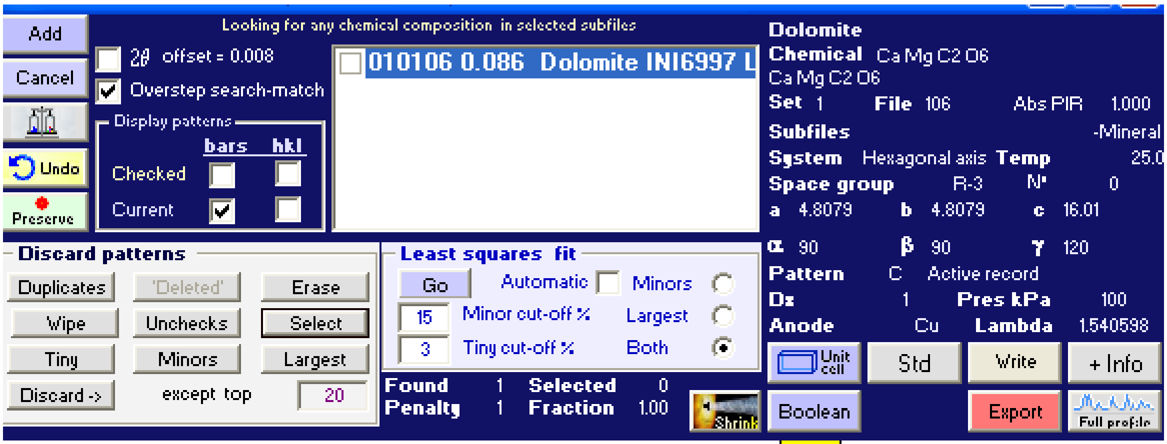


Figure 12.6. Expanded results display.



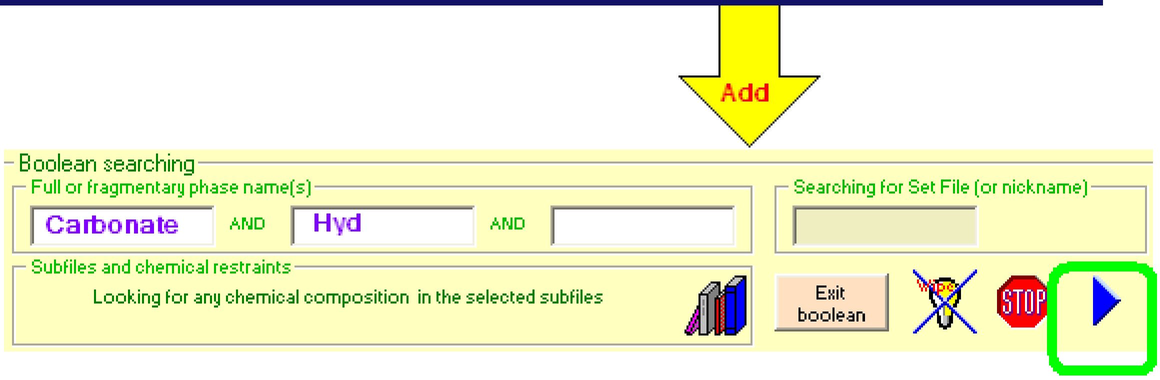


Figure 12.7. Boolean searching. In the example, every hydrated carbonate of the selected database will be added to the list, when the blue arrow button is pressed.

QUANTIFICATION USING DATABASES

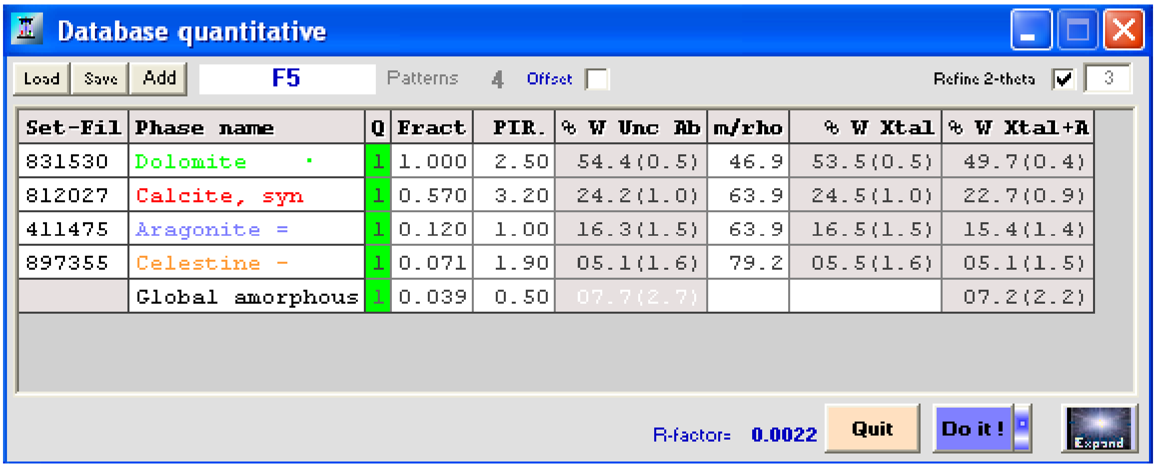


Figure 12.8. Quantitative analysis based on database records. Basic functions.

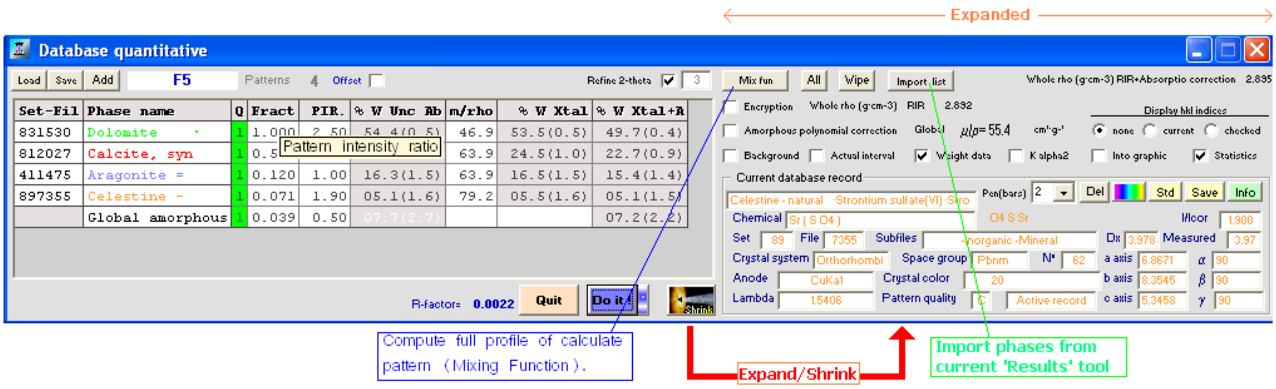


Figure 12.9. Quantitative analysis based on database records. Expanded functions.

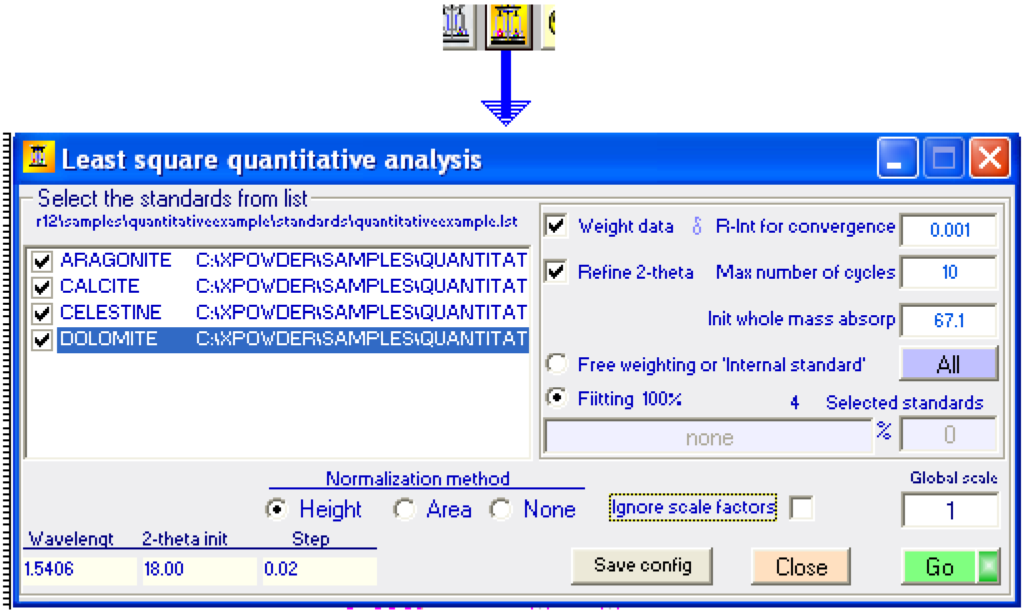


Figure 12.10. Tool for quantification using experimental standard patterns.

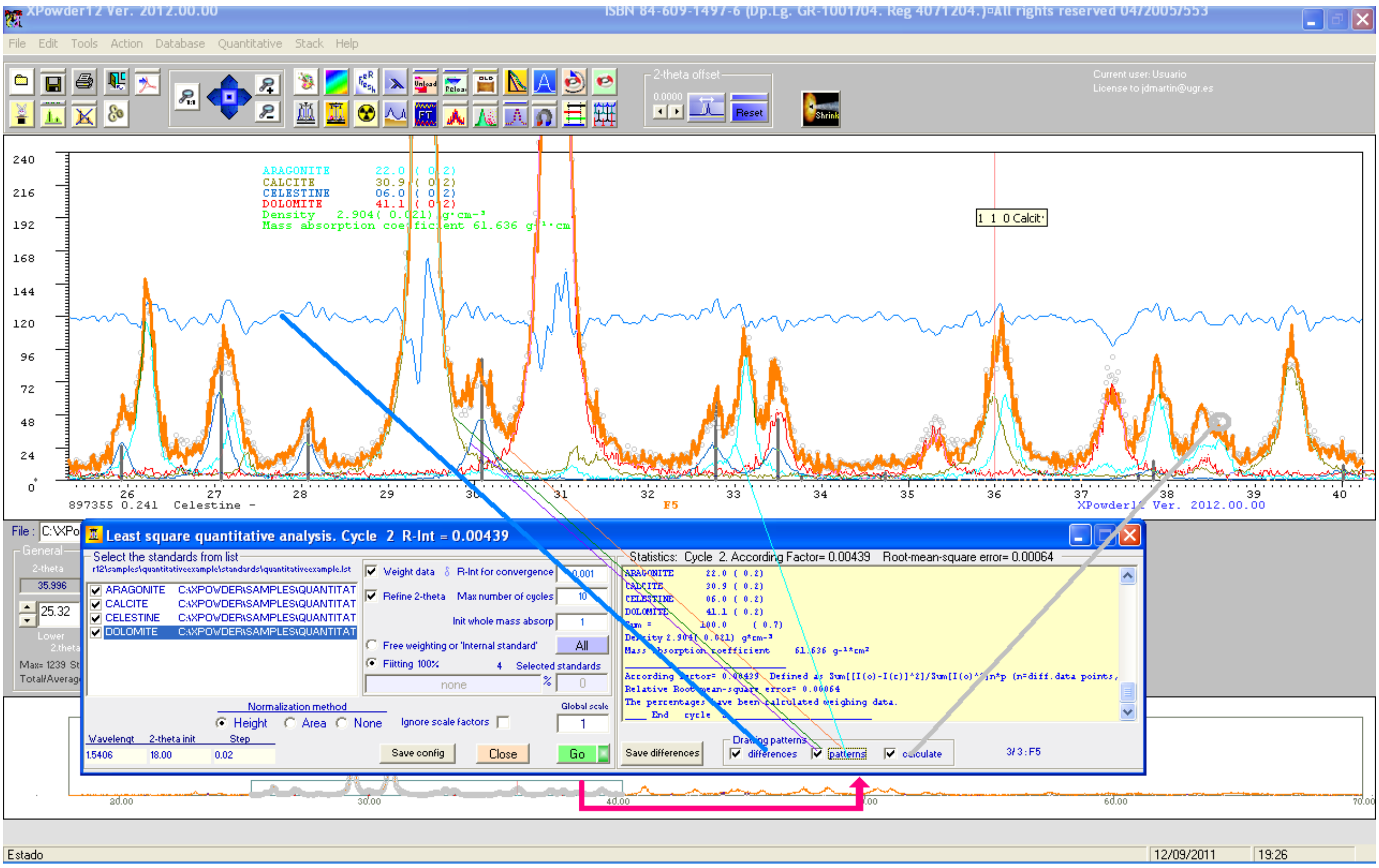


Figure 12.11. Quantification using the experimental standard pattern tool and results display (Note '*differences*', '*components*' and '*calculate*' display options).

Program window size

The program window size can be easily modified including the two following lines in the 'XPowder12.ini' file:

HeightScale = 'heigh scale factor'
WidthScale = 'width scale factor'

Where both scale factors may vary between 0,6 (60 % size) and 1 (full screen size).

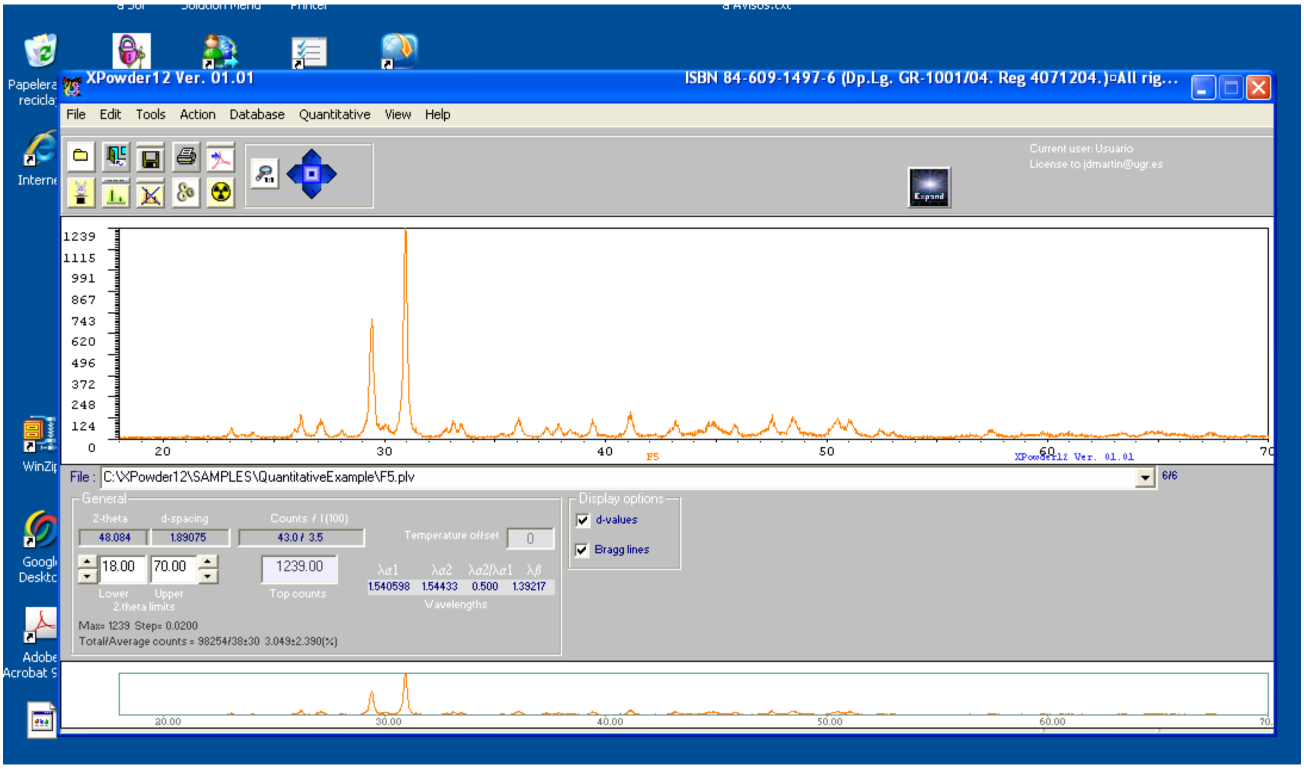


Figure 12.12. The example correspond to values of *HeightScale= 0.8* and *WidthScale= 0.9*

Transformation of 'Chemin' diffraction images to (x,y) text files

To access these functions simply open the image from the main menu:
File > **Open** /Select CHEMIN Images/ graphic file (*.TIF, BMP,JPG, etc).
The image of the diffraction spots is displayed as in Figure 12.13. Also, the initial parameters that define the width, height and sample-CCD distance which are included in the file *'XPowder12.ini'*, are shown in the top right of the screen. The initial coordinates of direct beam are referenced to the top left corner of the CCD. All units are in pixels and the values can be changed manually during the program execution. Additionally, some of these values, such as the coordinates of direct beam and the distance to the sample, can be tuned with various program tools.

The following actions may be performed:

1. Centering of the direct X-Ray beam on CCD.

There are three available methods (figure 12.13):

1.1. Select '**Customized centering beam**' (*Focusing manual*). It is only necessary to press the proper point. This method lacks precision, but can be used as a preliminary starting point.

1.2. *Auto Center* button. It usually works well, especially if you use previously 1.1.

1.3. **'Centering ring'**. When the option is selected, just click on any ring and it will focus on the direct beam. This is the most accurate method.

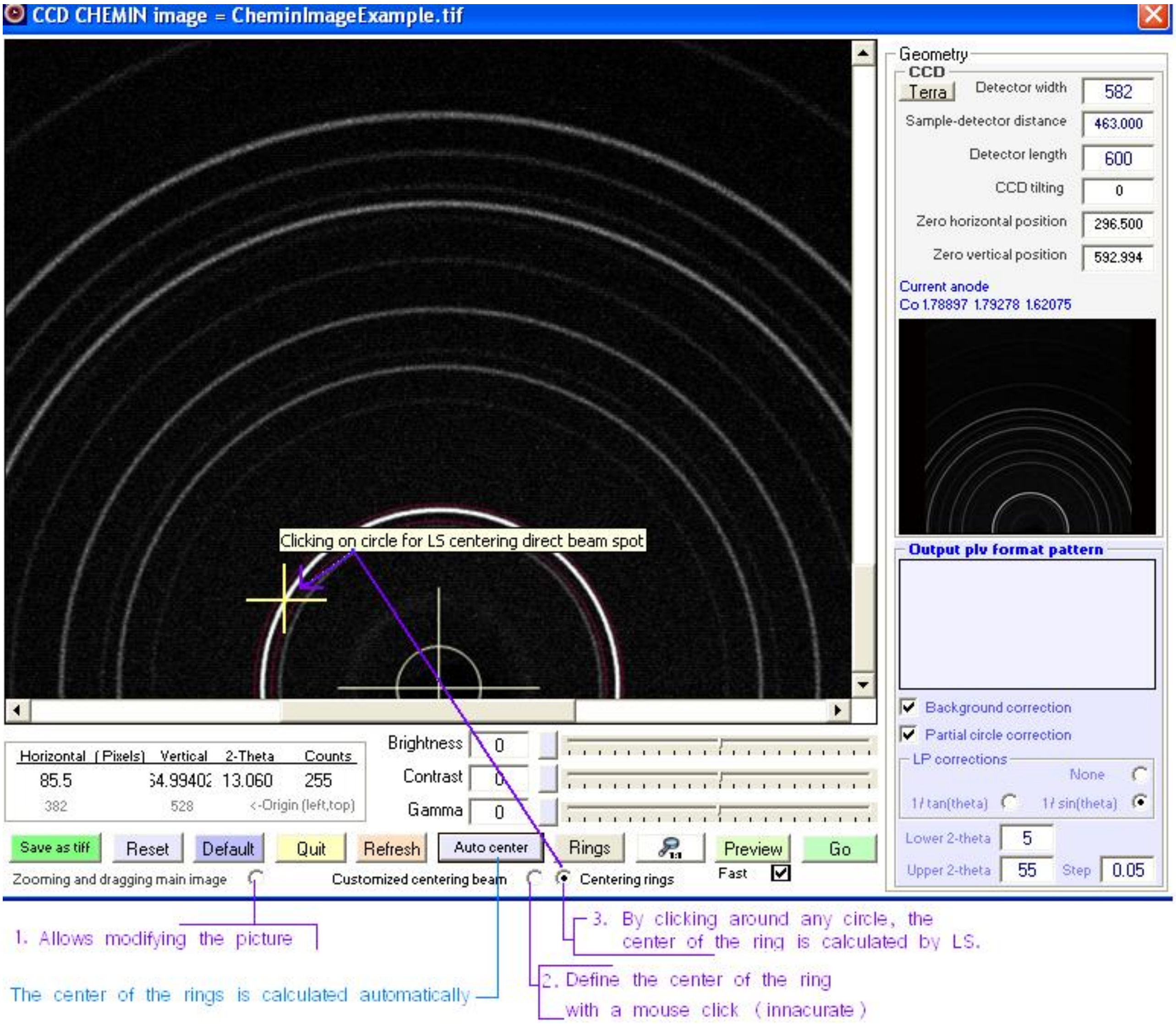
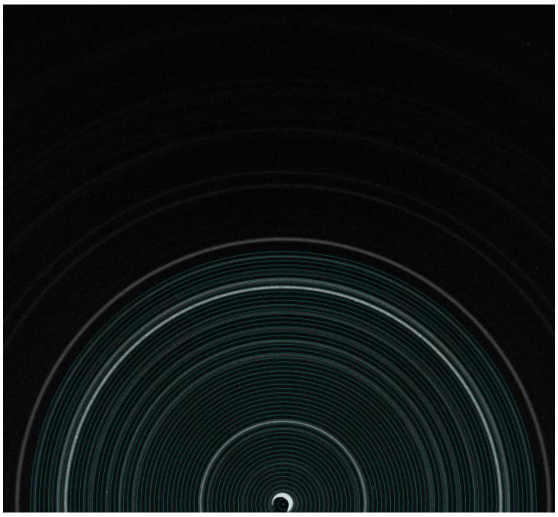


Figure 12.13. Diffraction image and main commands and features of the graphic tool.

The quality of the focus can be tested by pressing the button '**Rings**' (figure 12.14).



After having centered the direct beam it is advisable to mark the button **'Main image zooming and dragging'** to prevent the X-Ray beam center from accidental modification. Furthermore, this option allows you to move and zoom the image with the left mouse button and mouse wheel respectively.

Figure 12.14. Checking quality of the focus with the button 'Rings'.

2. Computation of (X, Y) data.

(X= 2θ°, Y= Accumulate counts at the ring of radius 2θ°).

The calculation is done with the buttons ('**Preview**' or '**Go'**, See figure 12.14). Several options can be used:

2.1. '**Partial circles correction**'. Fix the breakdown of the circles outside the boundaries of the CCD (recommended).

2.2. '**1/sin(theta)**' correction. Create a diffractogram as obtained from Bragg-Brentano geometry and *automatic slit* (recommended).

2.3. '**1/tan(theta)**'correction . This action computes an diffraction pattern similar to the previous one.

2.4. Background subtraction.

The 2θ limits and the 2θ step of the output diffractogram can be selected, as well as detector width, length, distance, tilting, etc of the device. Alternatively, 'Terra' diffractometer geometry can be used (button 'Terra').

The '**Go**' button sends the calculated diffractogram to the main screen (figure 12.15.).

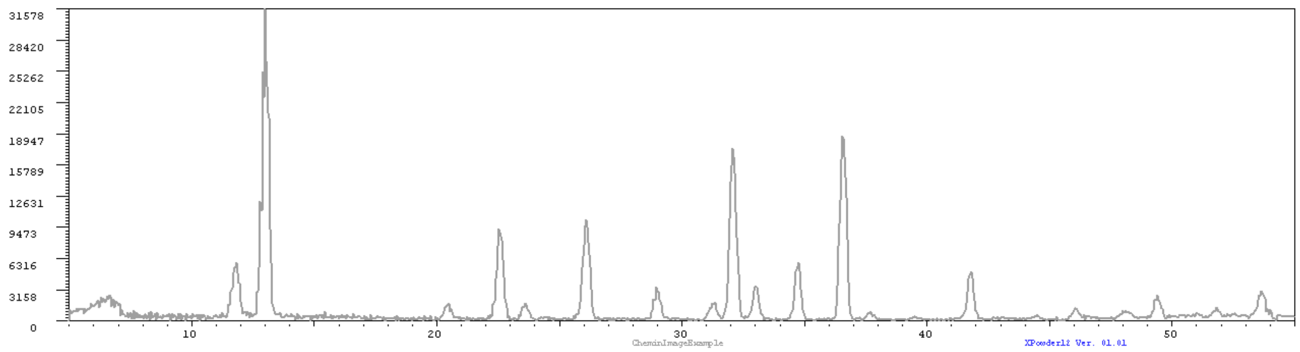
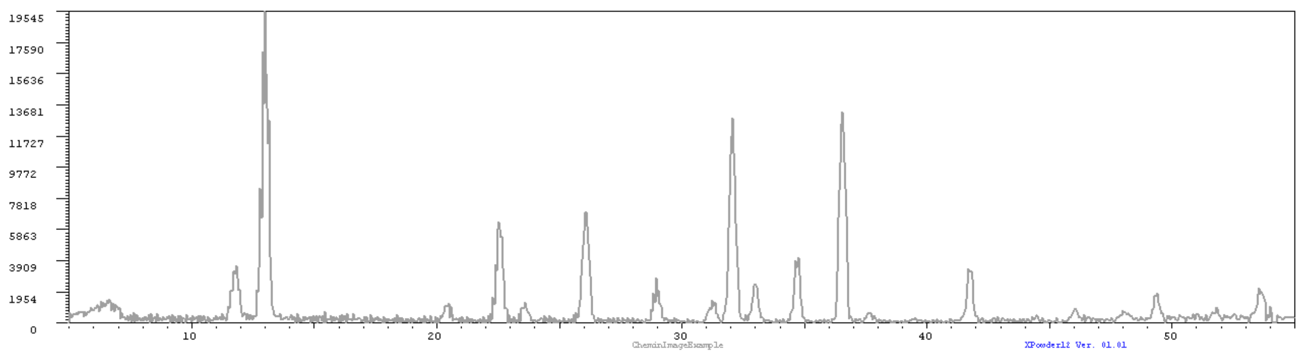
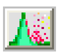


Figure 12.15. Computed diffraction pattern obtained from figure 12.13. containing $K\alpha_1$ + $K\alpha_2$ + $K\beta$ peaks. Background has been subtracted and intensities have been divided by *sinθ*, according to instructions of figure 12.14. In most cases, as in the example, it is



necessary to remove the $K\alpha_2$ (figure 12.17) and $K\beta$ (figure 12.18) components by using the commands of home menu (See figure 12.3.).

Figure 12.16. Pattern after having *Stripped $K\alpha_2$* ( in home screen).

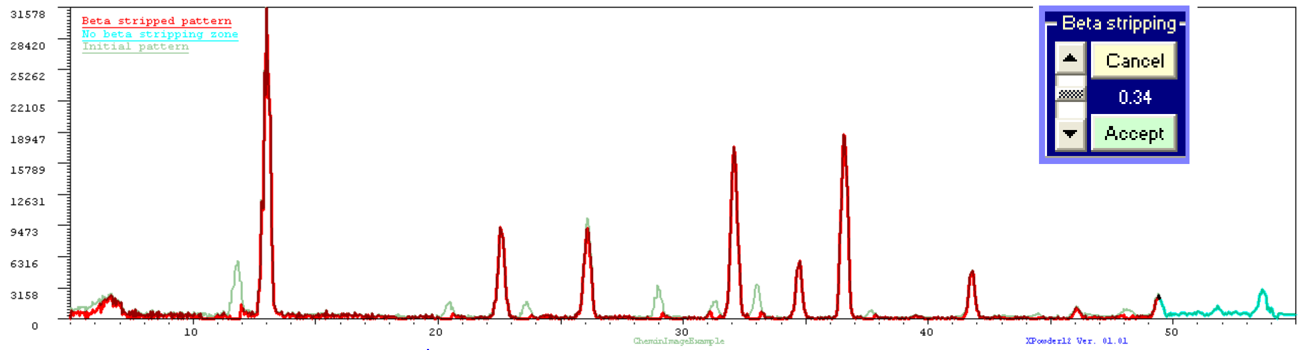


Figure 12.17. *β stripping* (in home screen). The (*IKβ : IKα1*) relation can be tuned with the vertical scroll bar of the figure. Original pattern shows in grey and *β-stripped* pattern shows in red. Final 2θ zone trace, in green, is unavoidably excluded from computation.

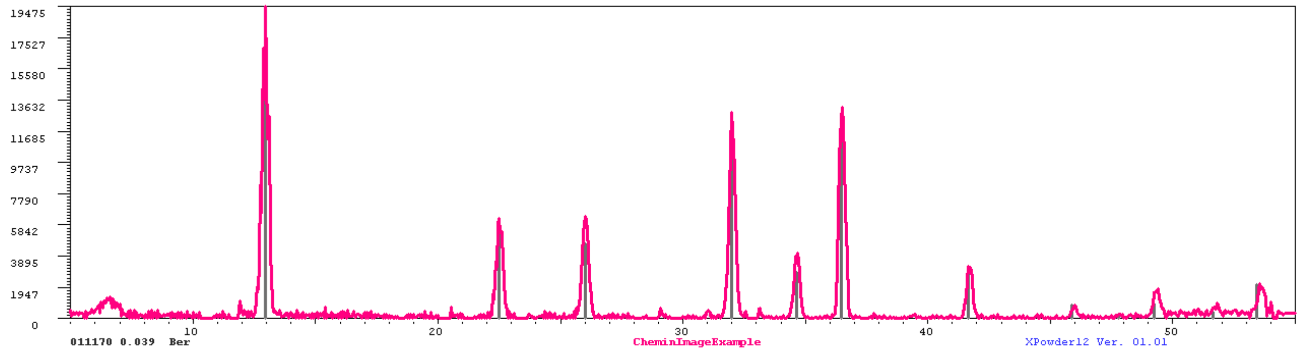


Figure 12.18. Pure $K\alpha_1$ pattern

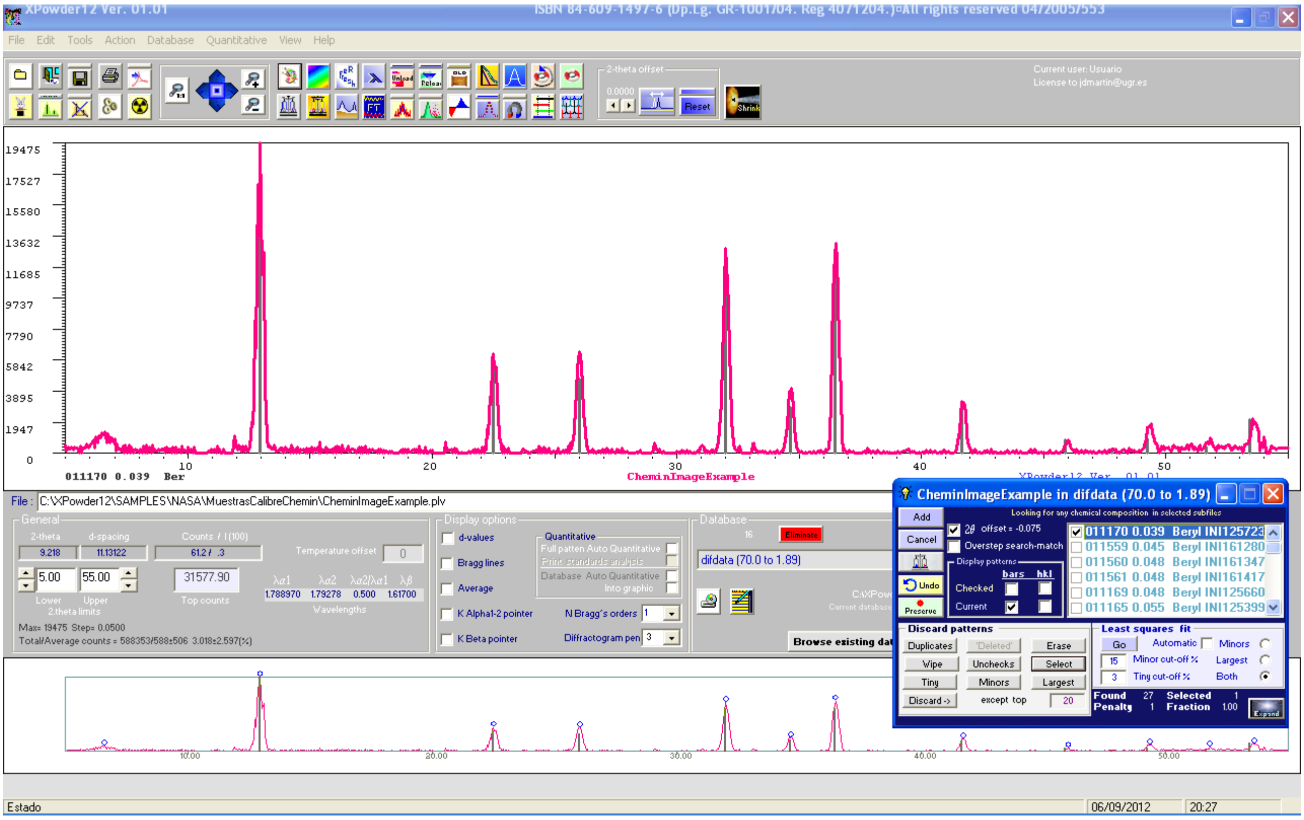


Figure 12.19. Applying *One-Click searching* on pattern from figure 12.17. The results list shows the beryl records of the database (AMCSD).

A new fast method for full-profile quantitative analysis of components using 'Dirac' patterns and convolution

XPowder12 ver 2012.02.02 or later.

This method consists on fitting full profile diffractogram to their components, either experimental or calculated by least square statistical methods, or simulated annealing. Additionally, PIR scale factors are used.

Where the components are calculated, they can be obtained from an experimental diffractogram of a highly crystalline pure compound, or one theoretical type 'Dirac' (see below). These diffractograms are referred to as 'starting pattern' or 'stick pattern'.

A 'model diffraction pattern' deconvolution with the 'starting pattern' is used to obtain the appropriate 'function filter' in order to obtain the final 'broadening pattern' of individual compounds. The 'model diffraction pattern' may be, for example, the diffractogram of any sample recorded in our laboratory.

The final 'broadening patter' of each component is then obtained by the convolution product of the 'stick pattern' with the 'function filter'. Optionally, you can add the Cagliotti broadening equation and/or correction for $K\alpha_2$ inclusion.

This 'broadening pattern' allows obtaining high quality quantitative analysis very quickly, as explained in detail in the attached example.

XPowder12 Quantitative Dirac...

XPowder12 Quantitative Dirac...

These files contain all data from a diffractogram, including the beginning angle, step, lambda, etc. All the intensity values are zero except for those corresponding to 2θ angles of the d-spacing of any phase (figure A1).

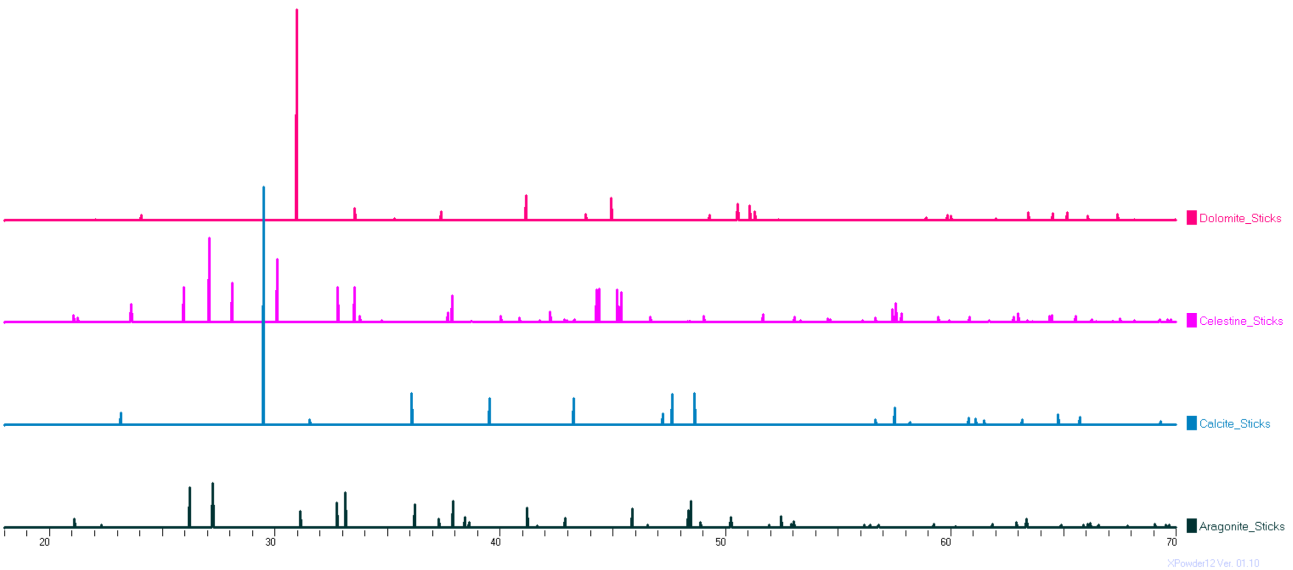


Figure A1.

The 'Dirac' button lead to generate these diffractograms from any card of an existing database (figure A2), or calculated from the space-group and unit-cell parameters (figure A3), or from the principal menu (Save File As...?, Figure A4), the selected values in an experimental diffractogram can be also saved in this special format also. Optionally, the corresponding to Kα_2 y Kβ reflections could be included.

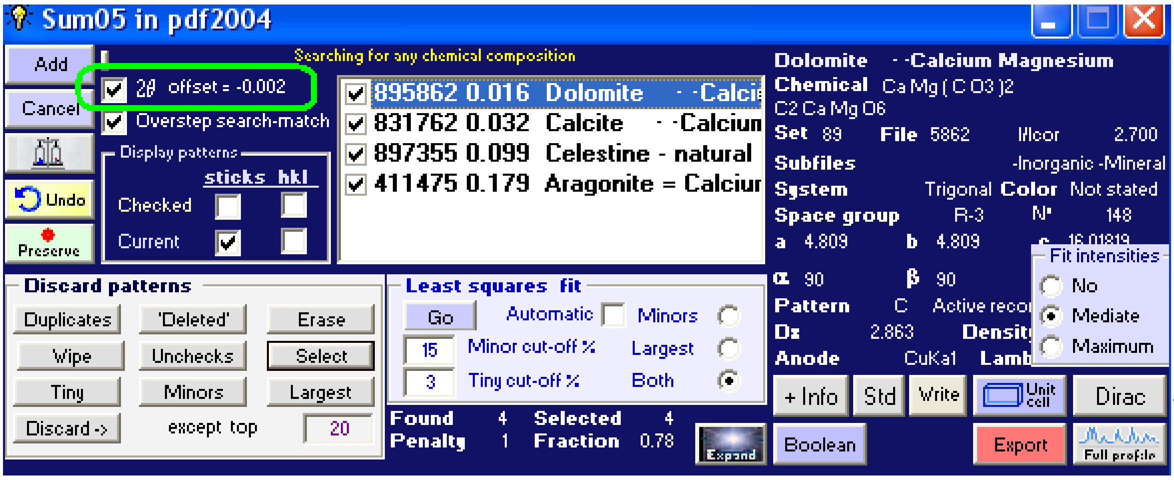


Figure A2.

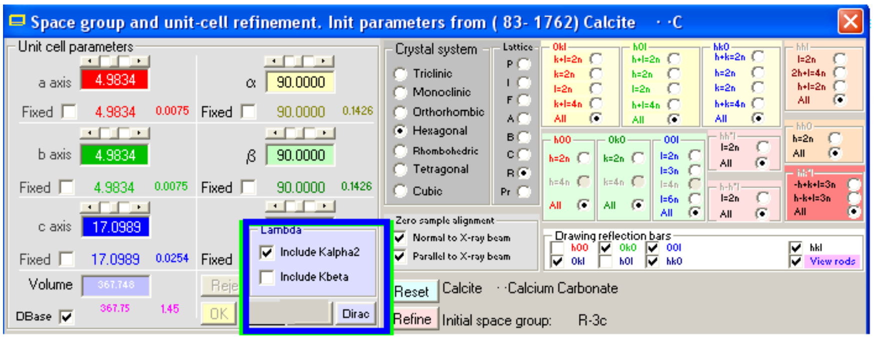


Figure A3.

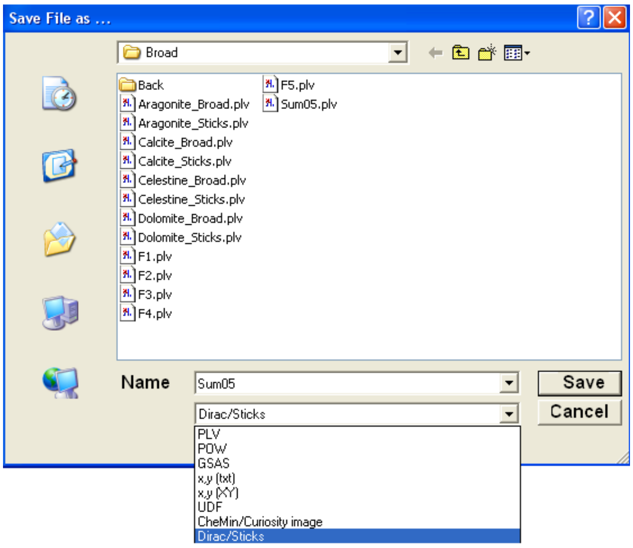


Figure A4.

These kinds of files could be used to simulate realistic experimental diffractograms of pure phases by convolution with distribution functions (Gauss, Cauchy, Pseudo Voigt, Pearson VII), asymmetry and FWHM computed by Caglioti equation.

XPowder12 Quantitative Dirac...

Broadening profile generation

Broadening profile generation from external diffraction pattern model

[XPowder12](#) [Quantitative Dirac…](#)

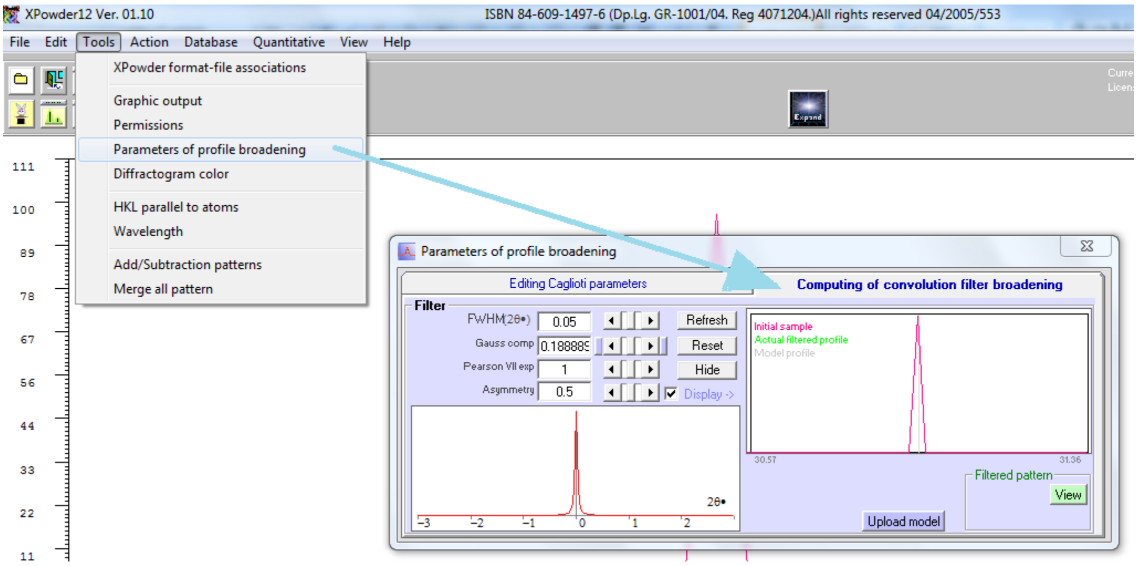


Figure B1. Initial filter (left, red) and 'Dirac' (purple) patterns.

This tool, located in the principal menu 'Tools' (Figure B1), allows creating any pragmatic theoretical profile by the modification of FWHM values, the Gaussian/Lorentzian components, the Pearson VII exponent and the asymmetry. If the 'Display' box is checked, the convolution product of this filter with the current experimental diffractogram will be displayed. The small screen on the right shows (in purple) the original diffractogram, Dirac in this case, on the selected 2θ interval.

When the cursor is positioned on the upper-right corner of the graphic, 'magnifying glass' and shift arrows are shown (figure B2). They allow us to focus and to shift the 2θ interval of the chosen reflection respectively.

The adjustment of the function filter can be done both manually, using the cursor (FWHM, Gauss, etc), and (or) automatically through an experimental or theoretical diffraction pattern model. This model can be any sample belonging to a batch that becomes capable of being quantified, and whose diffractogram has been recorded on our diffractometer.

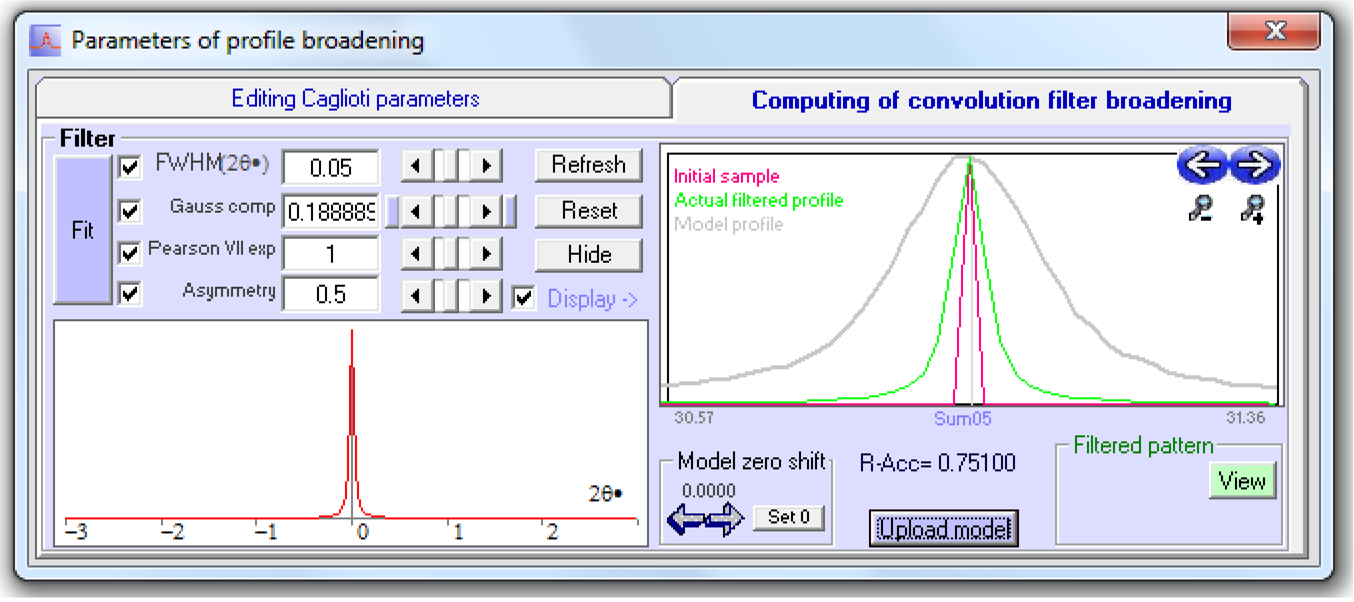


Figure B2. Initial filter (left, red), Dirac (purple), experimental model (grey) and preliminary convolution (green) patterns.

The tool 'Upload model' lead to load this model (in grey at figure B2) and adjust the 2θ position by 'Model zero shift' arrows.

The 'Fit' button is now available and allows obtaining automatically the correct filter function (red on the left of B2 figure). Equation [2] lets achieve the final pattern C (green in figure B3) by convolution with the principal 'Dirac' diffractogram (purple in figure B2). It would simulate the experimental conditions (including even the instrumental function as the sample parameters). The program uses *'simulated annealing'* methods, by the minimization of the ***R-Acc*** value, defined in the classic way.

$$\mathbf{R\text{-}Acc} = \sum_i w_i\,(Io - Ic)i \,/\, \sum_i w_i\, Io \qquad [1]$$

Where,
I = Counts of each pattern point (i), o = Measured counts, c= Calculated counts,
w = Statistical weight

The figure B3 shows the fitted final convolution product C in green.

$$\mathbf{C = A * B} \qquad [2]$$

Where
A= filter function

B= Theoretical diffractogram (Dirac) or experimental high crystallinity X-Ray pattern.
C= Final diffractogram fitted to the experimental lab conditions (grey).

The grey profile corresponds to any sample of our routine at the lab. It could be observed the concordance of this profile with the **C** calculated and the final **R-Acc** value (= 0.03073) enough small.

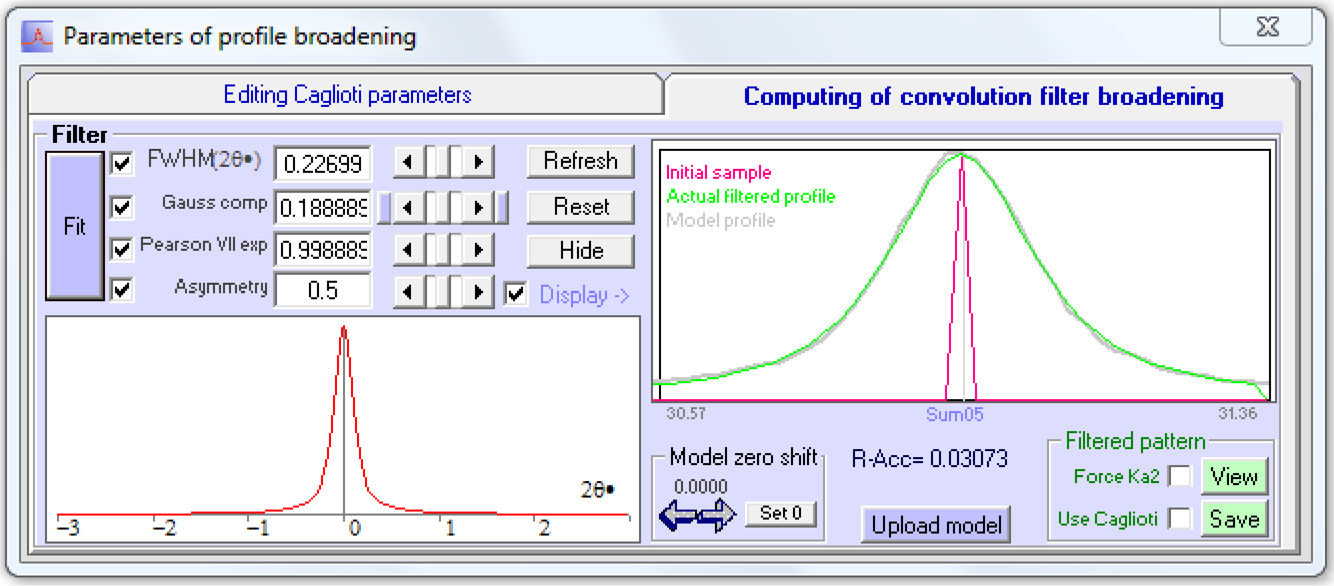


Figure B3. Clicking on 'Fit', the final broadened profile is computed. Notes R-Acc value (= 0.03073).

The button 'View' show the result of the convolution product in the principal screen as well.

The calculated diffractograms (C) could be saved (Save) including Caglioti FWHM adjustment and Kα_2 inclusion if case. Caglioti equation [3] parameters can be modified and edited in the tab 'Editing Caglioti parameters' (figure B4). For setting the initial U, V, W, P parameters, the 'pattern model' can be used as in chapter 11 of the XPowder user guide.

Now, the full calculated diffractograms (C) could be saved (Save) including Caglioti FWHM adjustment and Kα_2 inclusion, if case.

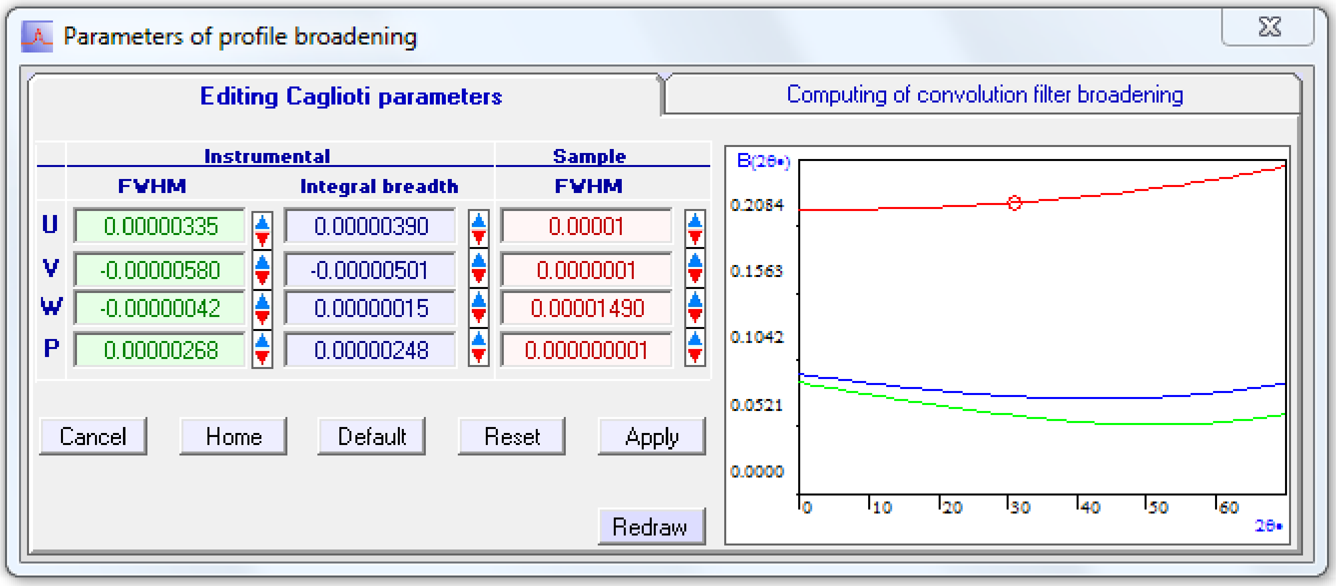


Figure B4. Caglioti functions for sample and instrumental profile. Small circle shows the position of the current profile.

The function to be applied on the calculation of the broadened profile is drawn in red. The small circle shows the position of the current profile used as a model for obtaining the convolution filter. The parameters U, V, W and P can be changed manually using the arrows (in 'Sample/FWHM' column). This action continually redraws the function. It should be noted that the change on the parameter **W** lets move the curve vertically, along the ordinate axis.

Caglioti equation: $$\mathbf{B}^2 = \mathbf{U} \bullet \mathrm{Tan}^2\theta + \mathbf{V} \bullet \mathrm{Tan}\theta + \mathbf{W} + \mathbf{P}/\mathrm{Cos}^2\theta \qquad [3]$$

(The values of **U**, **V**, **W** and **P** are calculated to express **B** value in 2θ radians. However this value is shown in the graph as 2θ degrees).

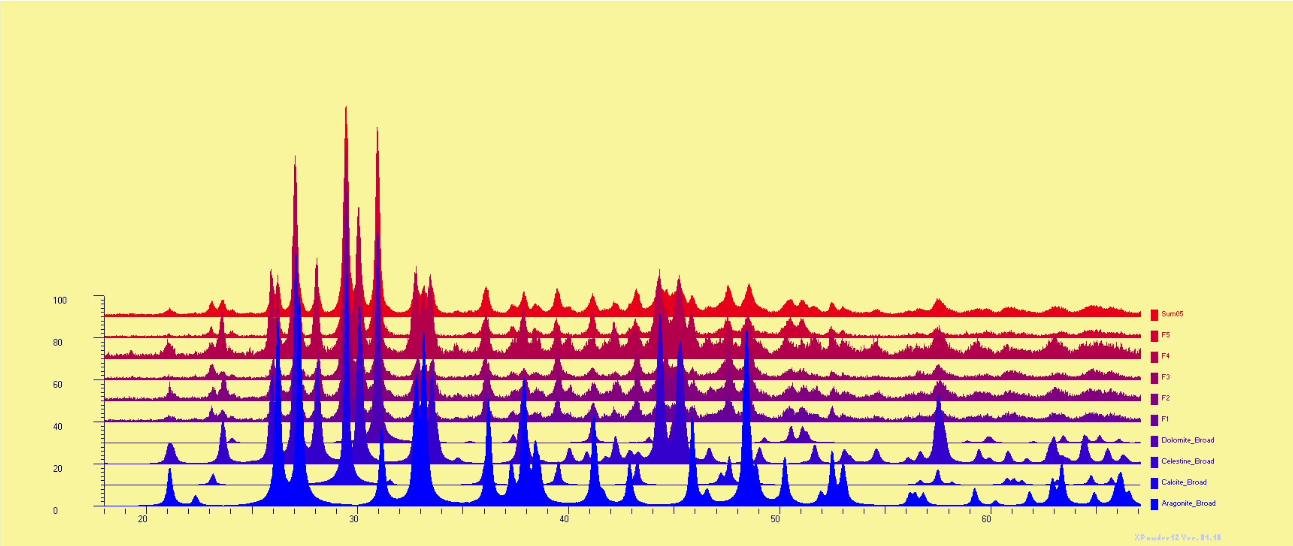


Figure B5

By this way, the theoretical diffractograms of Aragonite_Broad, Calcite_Broad, Celestine_Broad & Dolomite_Broad have been obtained and appear together with the diffractograms of experimental samples (F1, F2, F3, F4 y F5) and another one corresponding to the average (Figure B5). Now, the experimental samples may be quantified in terms of its theoretical component patterns.

XPowder12 Quantitative Dirac...

Extended practical example of uses of 'Dirac-Convolution' broadened diffractograms for accurate full-profile quantitative analysis of components.

XPowder12 Quantitative Dirac...

The examples to be used here are located in the 'Samples\QuantitativeExample' directory of the program. PIR scale factors are also calculated. It is recommendable for the user to check the following steps:

C.1. Upload diffractograms: F1, F2, F3, F4 & F5.

C.2. Identify the phases of any sample (F5 in the example)

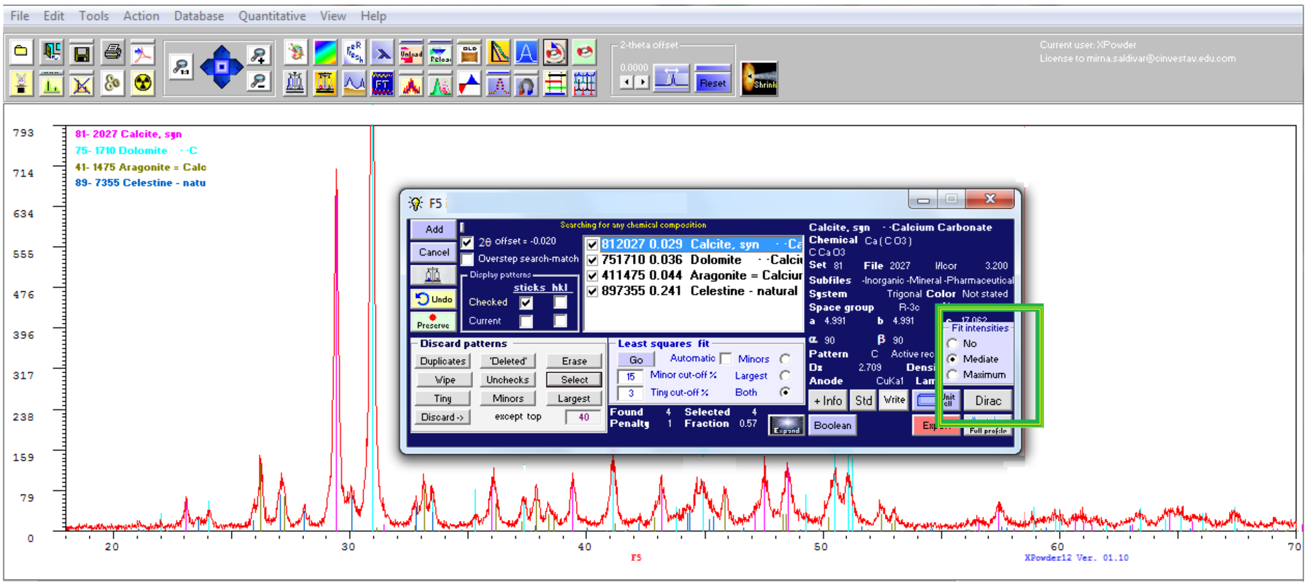


Figure C1

C.3. In Figure C1, Expand the tool and calculate 'Dirac' diffractograms for the components (*'Calcite_Sticks.plv'*, *'Dolomite_Sticks.plv'*, *'Aragonite_Sticks.plv'* and *'Celestine_Sticks.plv'*). The options 'No', 'Mediate' & 'Maximum' refer to the fitting between intensities of the experimental diffractogram (0, balanced, maximum respectively) and the database contained. In the example, the Mediate option is used.

C.4. Upload on turn the four components diffractograms (*'Calcite_Sticks.plv'*, *'Dolomite_Sticks.plv'*, *'Aragonite_Sticks.plv'* y *'Celestine_Sticks.plv'*), to apply in each of them the convolution filter and save the respective filtered diffractograms as in B. Thereby create the new patterns with suitable profile broadenings (*'Calcite_Broad.plv'*, *'Dolomite_Broad.plv'*, *'Aragonite_Broad.plv'* y *'Celestine_Broad.plv'*).

- Ideally, this is explained by only using the *'Dolomite_stick.plv'* pattern.

C.4.1. Select one isolated reflection of *dolomite_stick* (30.48 <2θ<31.43) in blue in the example

C.4.2. Upload model (e.g. sample F5, grey in Figure C2). It is advisable to use a model in which the background has been subtracted before. In the example the original sample without any modification is used. In some case, it might be necessary to modified by hand the zero of the model using 'Model zero shift' tool.

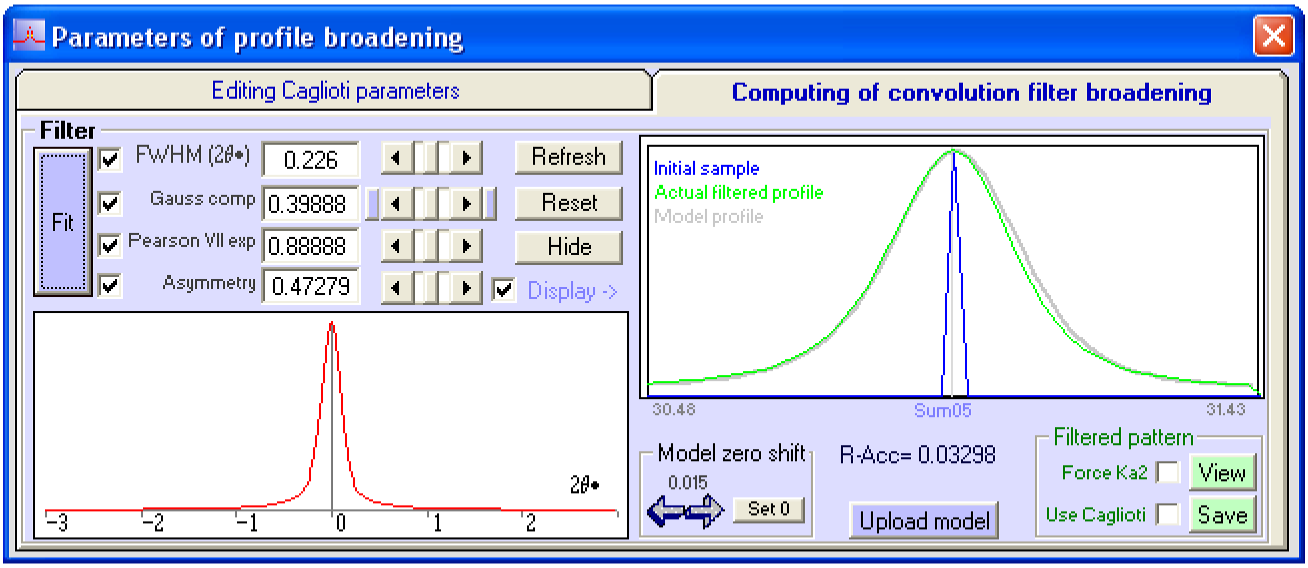


Figure C2

C.4.3. Click 'Fit' in order to calculation of broadened pattern. The result appears in green on figure C2 with ***R-Acc*** = 0.03298.

C.4.4. 'Save' -> (*'Dolomite_Broad.plv'*). The full final pattern is on figure C3. Figures C4 and C5 show other patterns involved in the example.

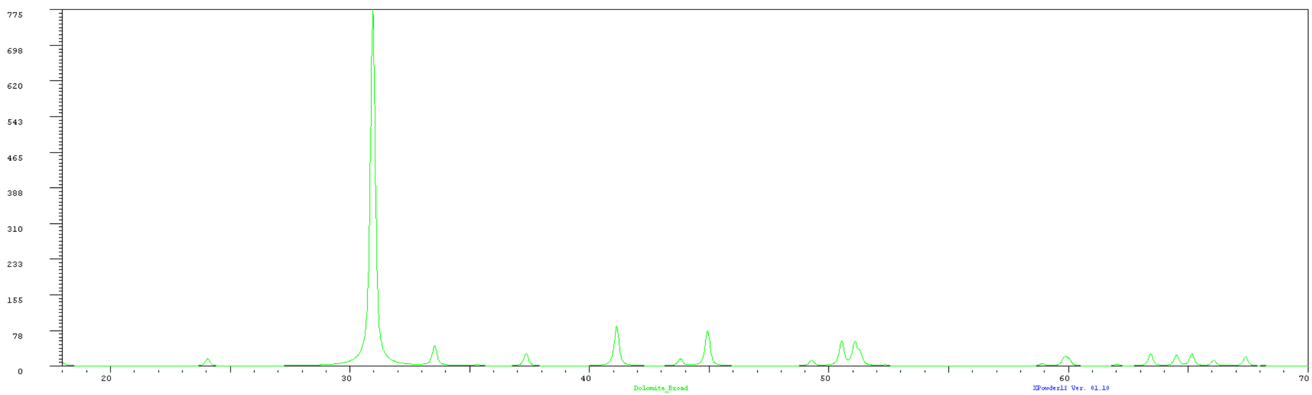


Figure C3.

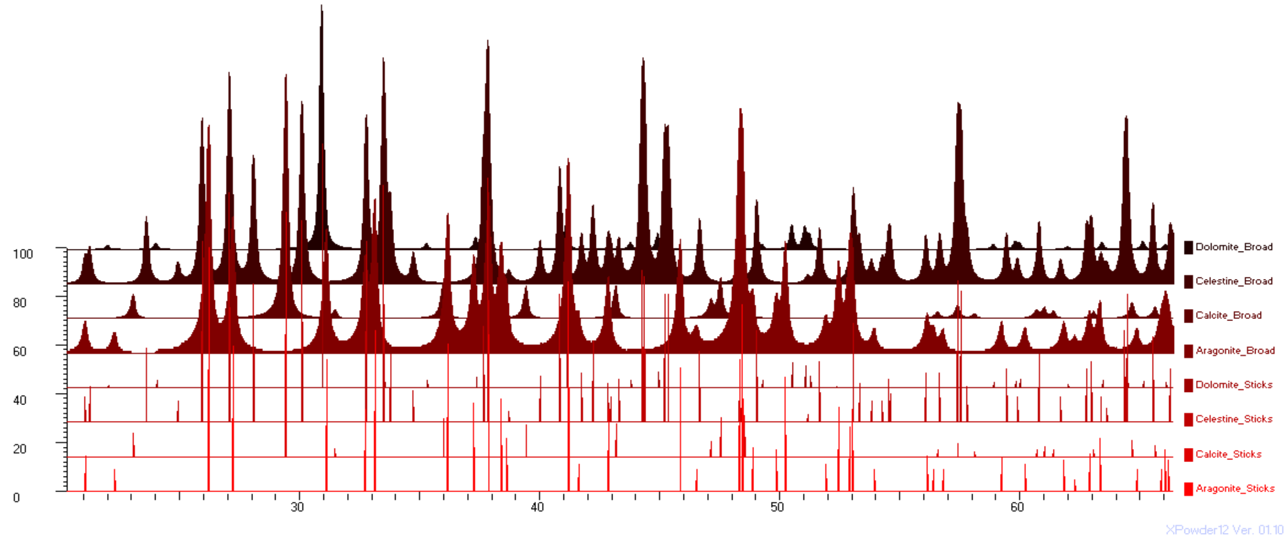


Figure C4. The figure shows the individual XRD patterns of the components, both initial (Sticks) and final (Broad).

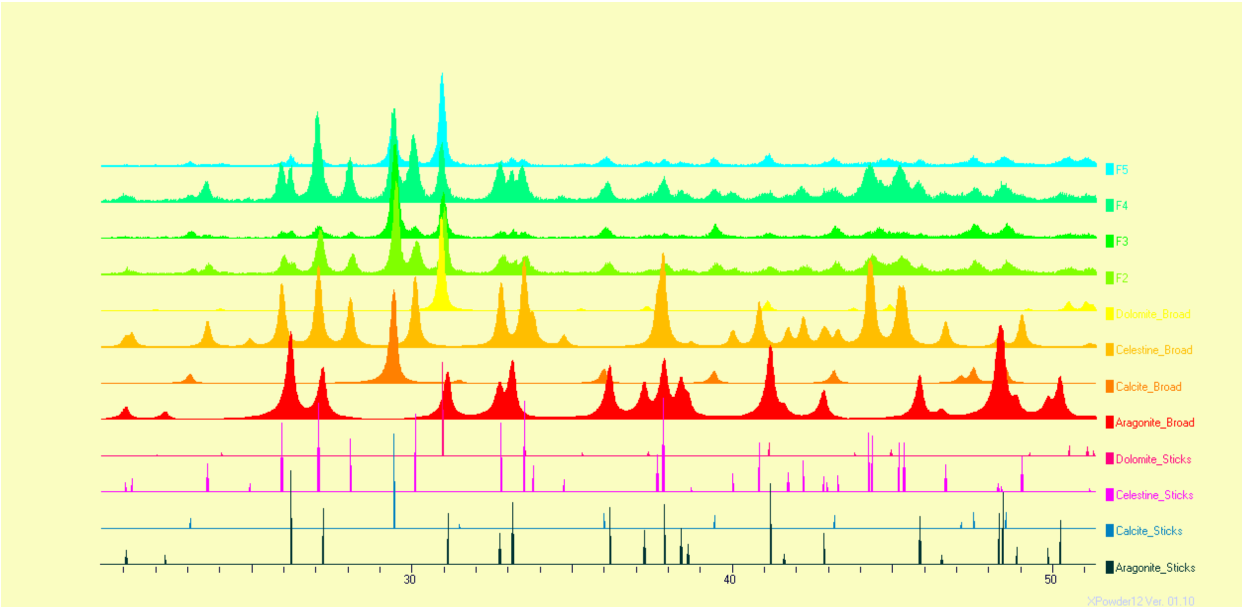


Figure C5. The figure shows all the patterns involved in the procedure. F1, F2, F3, F4, F5 are the samples to be quantified. 'Xxxx_Broad' are the broadened patterns of components. 'Xxxx_Sticks' are the '*Dirac/d-spacing*' pattern components.

C.4.5. Now, you must create a list within the standard patterns in the quantitative tool, using 'Examine' for each phase, as in figure C6. At the end, it is necessary to save this list with any name (eg 'ListOfPhases.LST').

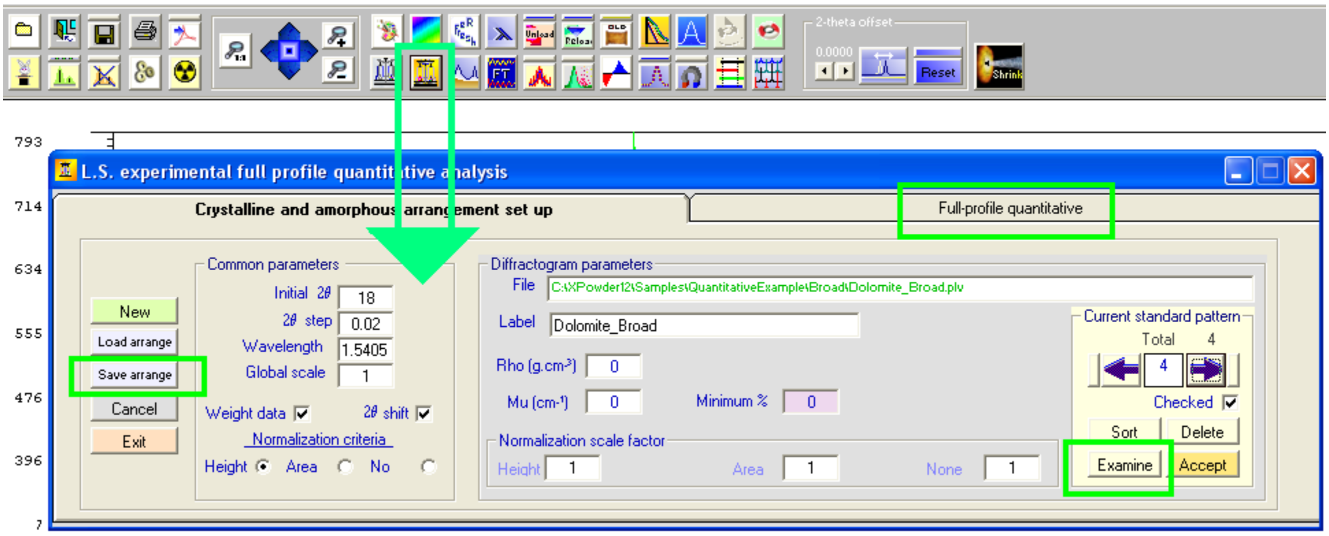


Figure C6. Quantitative tool: Building a list of standard patterns.

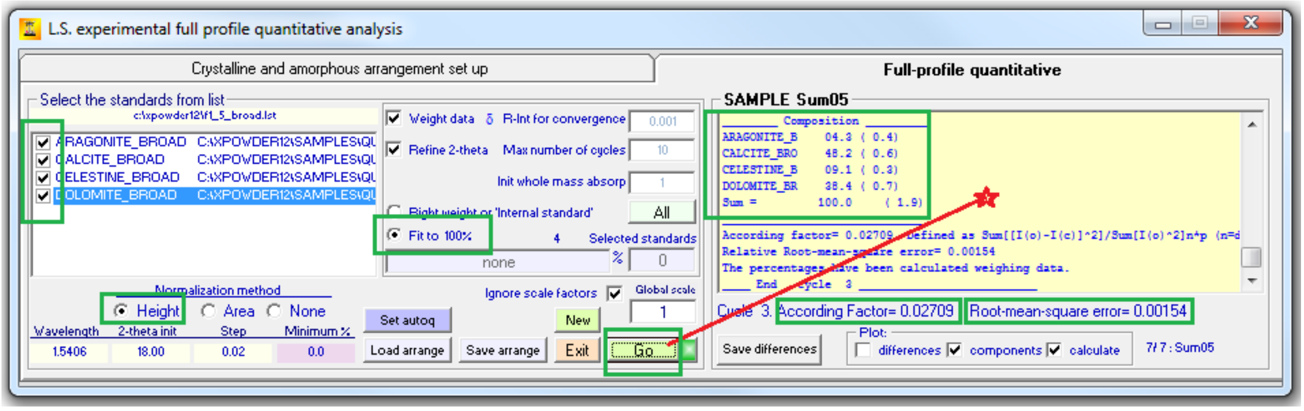


Figure C7. Preliminary quantification ignoring scale factors (RIR, PIR, I/Iref in other authors of places this manual user). All scale factors are set to 1.

C.4.6. Now, we carry out a previous quantitative analysis of **a known composition sample** (it could be created artificially), marking the 'Ignore Scale factor' cell. It could be done for any normalization criteria. In the example is used the statistical criteria 'Height'. Optionally any other criteria could be used (Area or None).

C.4.7. Results of preliminary quantification are showed in the figure C8. Optionally, the experimental sample could be showed together with the partial components (with different colors), differences (no in the figure C8) and calculate diffractograms (grey circles). The determination error is expressed by parentheses, just after each percentage, and it affects to the last significance numbers.

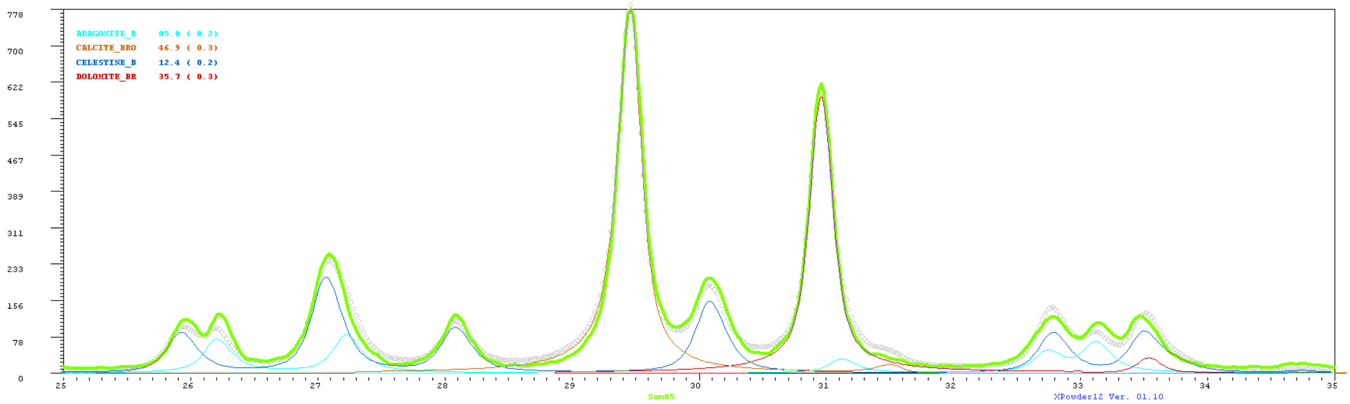


Figure C8. Quantitative decomposition of phase components in experimental sample *Sum5*. Circles are the calculated pattern.

C.4.8. Now is necessary to calculate the scale factors (PIR= Pattern Intensity Reference) by an easy calculation:

$$\text{PIR} = (\mathbf{X}_{1P}/\mathbf{X}_{1S}) \cdot (\mathbf{E}_S/\mathbf{E}_P) \qquad [4]$$

Where,

X_{1P} is the % of the phase used as reference (the most stable of the group)

X_{1S} is the % calculated for each one of the rest of the components

E_S is the % known of the reference phase

E_P is the % in the known weight of every one of the other components.

Obviously, the PIR value for the reference phase ('celestine' in the example) is '1' in all normalization criteria cases. However, it can be seen that an external weighed standard (like 10% corundum, 15% quartz,...) that allows application of these factors to extend to samples with different compositions can be added to this sample of known composition.

Take into account that the reference component could be added artificially to all samples (for example a 5% in weight). This allows the final quantitative analysis without the necessity of fitting the total to 100%.

In the last three columns on the chart of the following calculation, the PIR factors calculated by the three normalization criteria are reflected. The inclusion of the complementary data *Rho* and *Mu* (in figure C6) allows the absorption corrections and the media theoretical density calculation of the sample (no here).

Table C1.   S = Standard, P = other phases

PIR= $(X_{IP}/X_{IS})\cdot(E_S/E_P)$	X(with 'Ignore Scale factor')			Real % weight	Complementary data			PIR		
	$Height_I$	$Area_I$	$None_I$	E (% , mg, etc)	μ/ρ ($cm^2\cdot g^{-1}$)	ρ ($g\cdot cm^{-3}$)	μ (cm^{-1})	Height	Area	None
Aragonite	10.50	39.70	49.80	20.50	53.4	2.927	156.30	0.45	0.56	0.85
Calcite	98.60	45.80	89.00	35.30	63.9	2.711	173.23	2.46	0.37	0.88
Celestine (Standard)	26.00	79.90	65.70	22.90	79.2	3.978	315.06	1.00	1.00	1.00
Dolomite	75.00	33.50	76.60	21.30	46.9	2.863	134.27	3.10	0.45	1.25

FINALLY, THE PIR *NORMALIZED SCALE FACTORS* IN THE MODEL (FIGURE C6) MUST BE INTRODUCED AND THEN THE LIST HAS TO BE SAVE AGAIN AS IN C.4.6. THIS LIST WOULD BE USED AT ANY TIME TO ANALIZE ANY NUMBER OF SAMPLES IN 50 SAMPLES GROUPS. TO INDICATE THAT THE MODEL GENERATION COULD SEEM COMPLICATED AT THE BEGINNING. AT SOME POINT THE USER WILL REALIZE THAT IT IS NOT.

This list can be used in AUTOMATIC MODE (AUTOQUANTITATIVE). To do this you need to edit the file and enter the lines:
[Standard quantitative]
StAutoQuantitative= c:\xpowder12\ListOfPhases.LST
StQuantitative_StEnabled= True *(or False case NOT AUTOQUANTITATIVE)*
You can also do this from the program (Use 'Set autoq' button of figure C9)

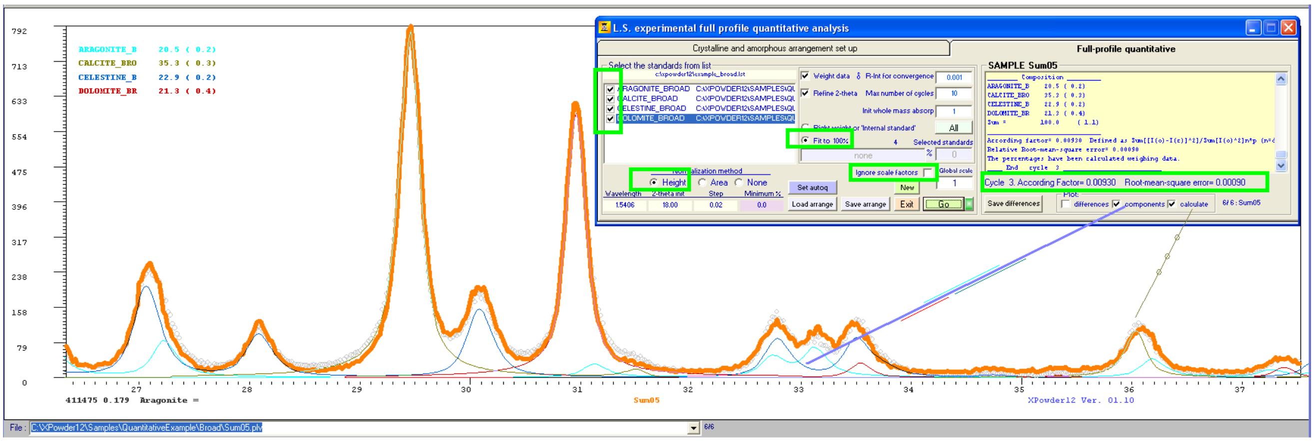


Figure C9. Final model is completed. Now, all samples can be routinely analyzed one by one way (Go) or in clusters ( ) of up to fifty.

THE CREATED MODEL IN THE EXAMPLE HAVE BEEN DONE IN HALF AN HOUR APROXIMATELLY AND NOW IT COULD BE USED AFTERWARDS, AT ANY TIME, IN A CONTINUATED WAY IN INDUSTRIAL CONTROL PROCESS, MINNING AND QUARRING, BASIC INVESTIGATION, ETC.

The output of results can be saved using '*File/ Save Log File as TXT*' on home screen.

Also, it can be saved as PDF using  (upper bars for all upload samples, lower button for current sample).

The table below shows a part of the report generated for the samples analyzed here. All these examples are incorporated diffractograms of the program (*XPowder12ProgramDir*\Samples\QuantitativeExample).

Table C2

Sample	*	ARAGONITE	CALCITE	CELESTINE	DOLOMITE	Rho(g.cm-3)	Mu(g-1·cm2)	Rint	Cycles	Sigma
F1	*	19.7(0.2)	39.7(0.3)	20.0(0.3)	20.7(0.4)	0.000(0.000)	0.000	0.01257	2	0.00097
F2	*	17.2(0.3)	33.2(0.4)	31.8(0.3)	17.8(0.5)	0.000(0.000)	0.000	0.01497	3	0.00104
F3	*	15.7(0.2)	52.3(0.3)	13.7(0.2)	18.3(0.3)	0.000(0.000)	0.000	0.00940	2	0.00092
F4	*	25.5(0.5)	22.4(0.8)	41.8(0.5)	10.4(1.0)	0.000(0.000)	0.000	0.02629	3	0.00136
F5	*	22.6(0.2)	30.4(0.3)	06.5(0.2)	40.5(0.2)	0.000(0.000)	0.000	0.00915	3	0.00089
Sum05	*	20.5(0.2)	35.3(0.3)	22.9(0.2)	21.3(0.4)	0.000(0.000)	0.000	0.00930	3	0.00090

Sum fitted 100%. The percentages have been calculated weighing data. 2-theta angles have been refined
Normalization criteria: Max. counts = 1

XPowder12 Quantitative Dirac...

P2D2 DATABASE

Predicted Powder Diffraction Database

The P2D2 (Predicted Powder Diffraction Database) is built up by calculating the powder patterns corresponding to the predicted crystal structures from the latest **PCOD update**. The job is done partly by **ZEFSA II** (898707 entries) and for the **GRINSP** data (163520 entries) by the CIF2POW software. The P2D2 database currently includes twelve text files, each with approximately 100000 compounds, which can be automatically indexed by XPowder12, individual or jointly.

These files are:

Zeolites BKS data (Two different clusters can be created, each containing three BKS files)

P2D2-BKS01.txt Tetrahedral only (100000 entries each)

P2D2-BKS02.txt

P2D2-BKS03.txt

P2D2-BKS04.txt

P2D2-BKS05.txt

P2D2-BKS06.txt

Zeolites SLC data (The four SLC files can be grouped into a single cluster)

P2D2-SLC01.txt Tetrahedral only (100000 entries each)

P2D2-SLC02.txt

P2D2-SLC03.txt

P2D2-SLC04.txt

GRINSP data (The two GRINSP files can be grouped into a single cluster)

P2D2-GRI01.txt Zeolites and frameworks with one sort of polyhedra, ~60000 entries

P2D2-GRI02.txt Structure candidates combining two kinds of polyhedra, titanosilicates, etc, ~100000 entries

Also, the four SLC and the two GRINP files can be grouped into a single cluster, but about 1% of the patterns may be remain unindexed. To group the all six BKS files in a single cluster, it is necessary to limit the scan interval in a specific database setup, so that this left optimized in function of the experimental conditions in our laboratory (i.e. limiting d-spacing interval between 70 to 2.5 Angstroms).

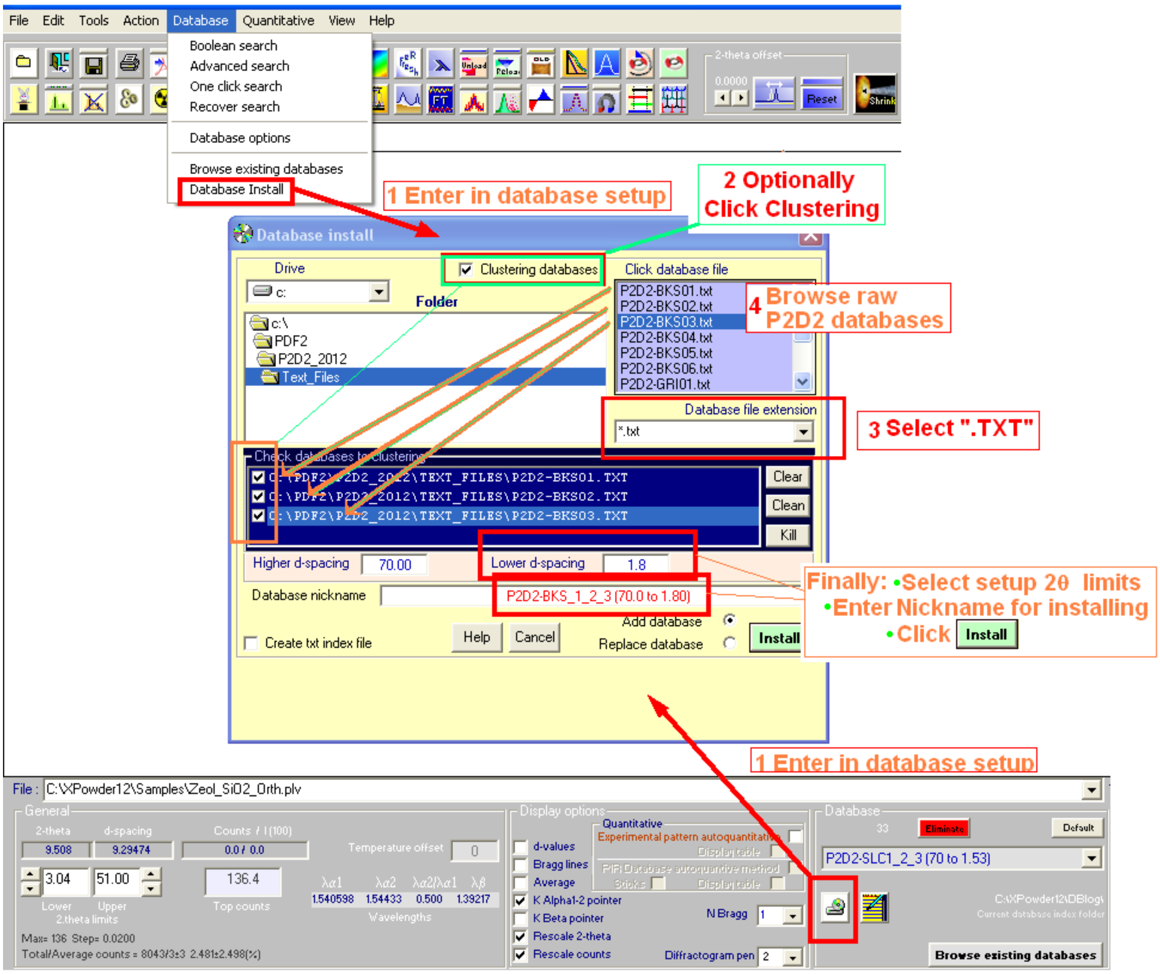


Figure D1. P2D2 database setup. Several files can be grouped into a single database by checking the 'Clustering database' box (see also previous page).

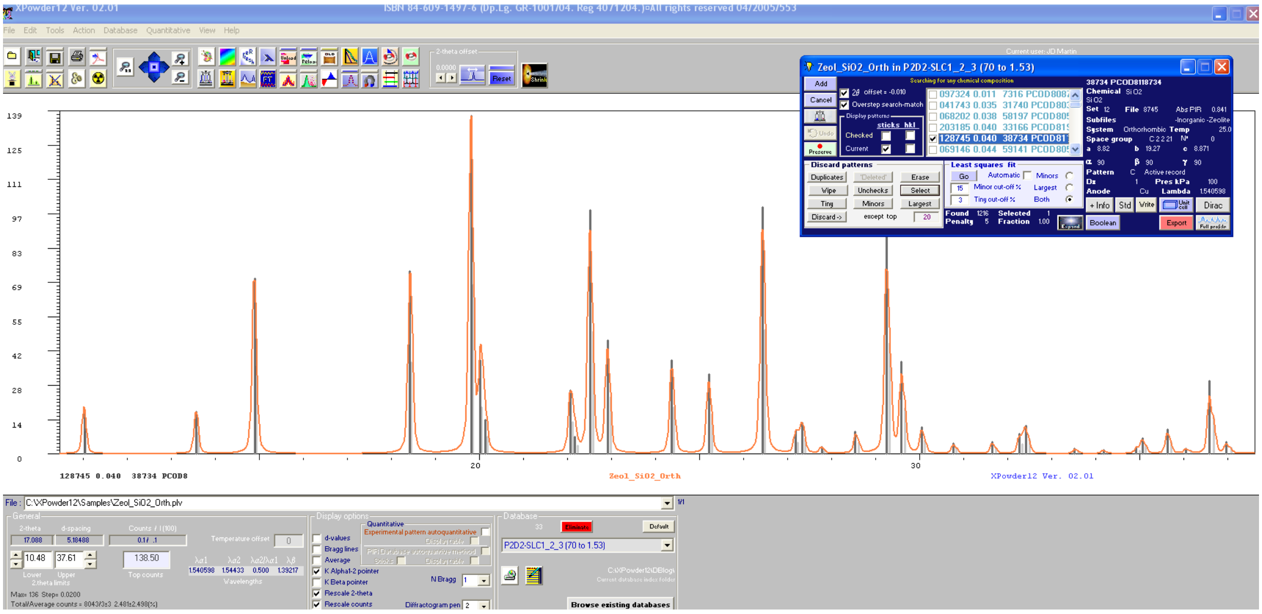


Figure D2. 'One Click' search-math checking with a cluster of P2D2-BKS01, P2D2-BKS02 and P2D2-BKS03 files (300 000 entries of P2D2 patterns).

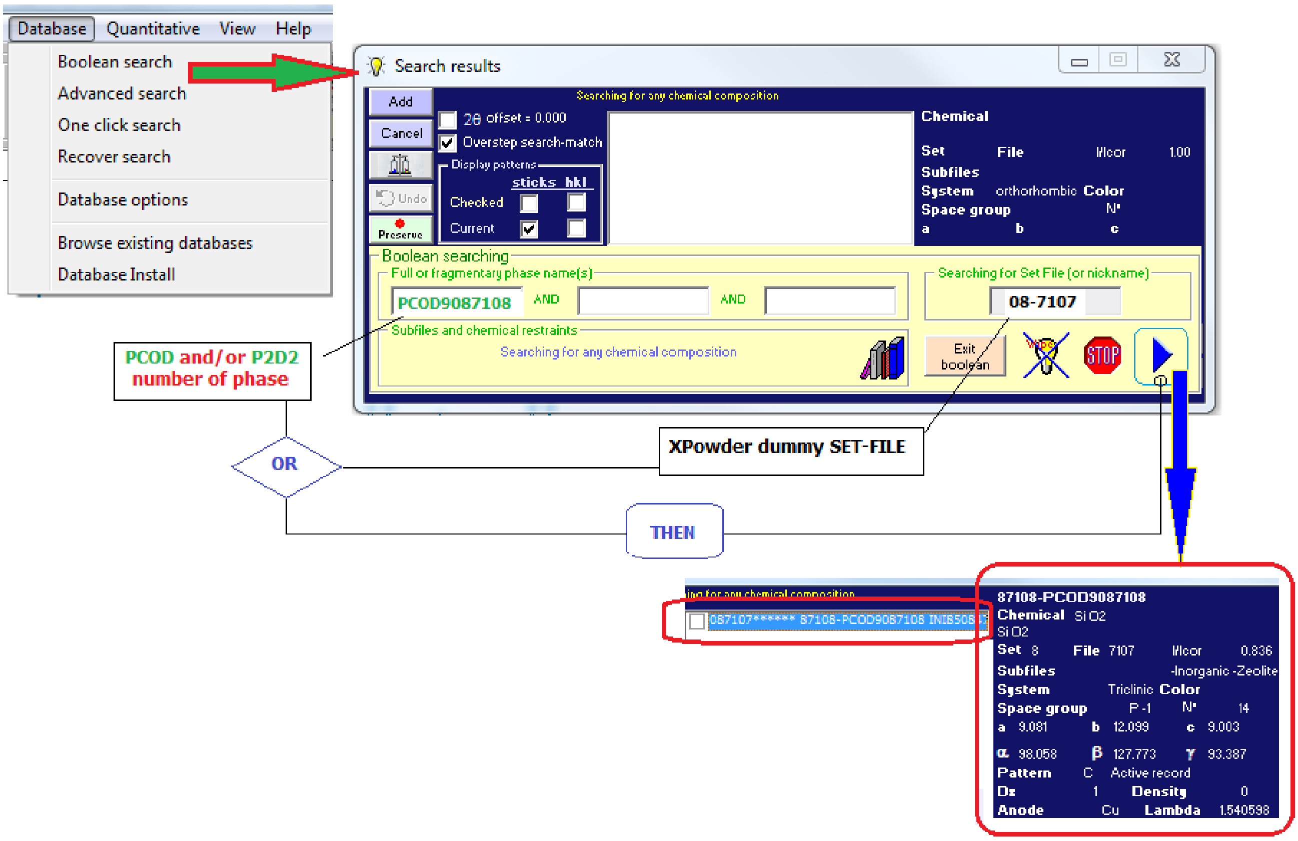


Figure D3. Boolean searching in P2D2. In the example, 9087108 PCOD phase is displayed by entering their code. 'PCOD9087108', '9087108', '908' AND '7108' can be used indistinctly. SET & FILE are XPowder12 dummy codes for PDF2 compatibility purposes.

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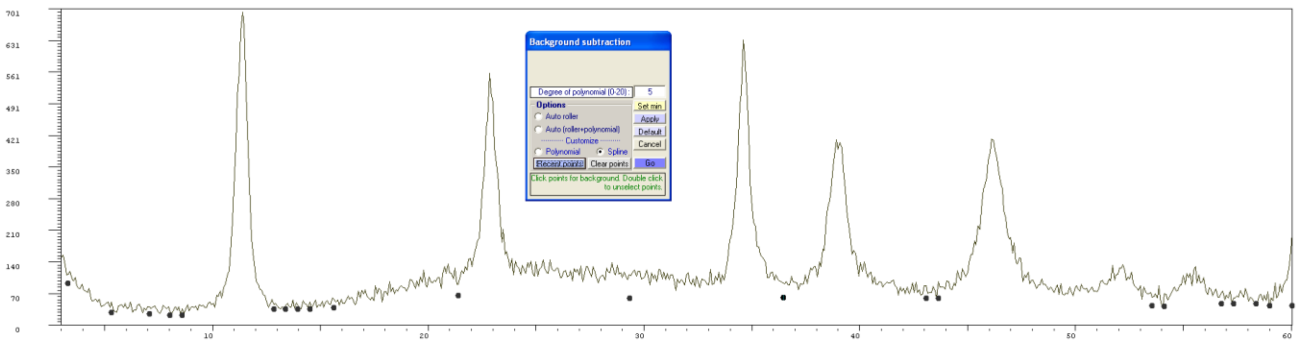
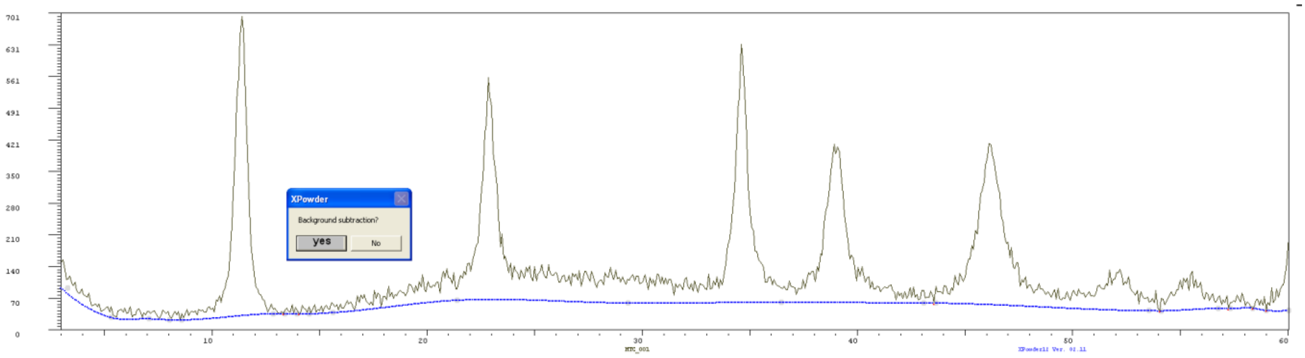
New additional method for background subtraction

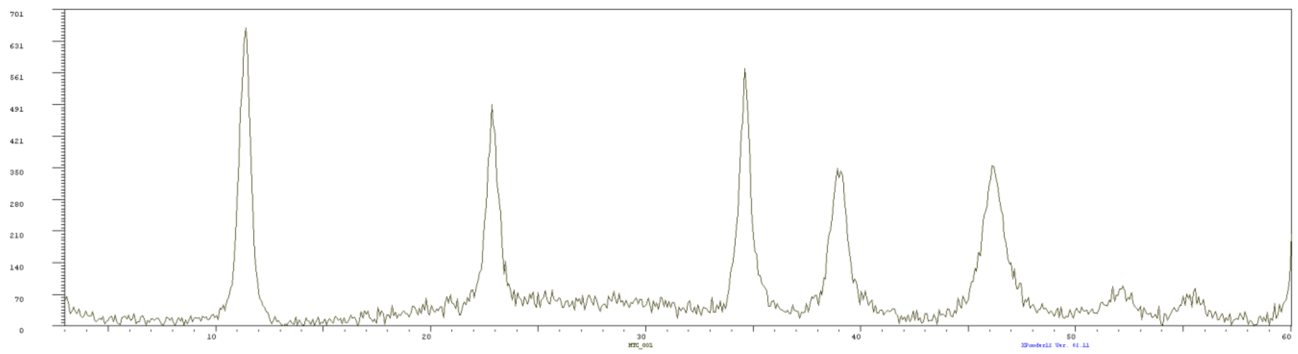
The custom points where the background will be plotted, can now be adjusted by an cubic spline in addition to classic polynomial fitting.



A） Select custom background points and ‘Option spline’



B） Clink ‘Go’ and select ‘yes’

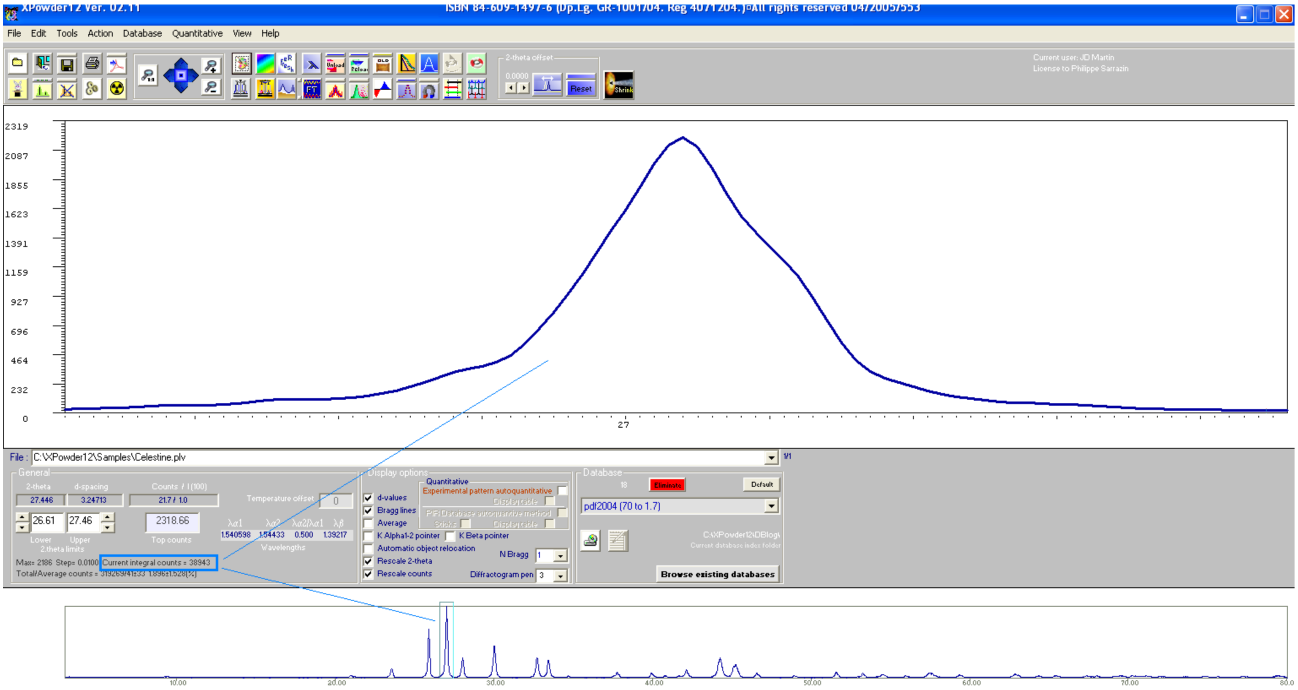


C） Background correction is done.

XPowder12

New topics ...

Ver XPowder12.02.11



The area under the selected zone is now displayed continuously.

Ver XPowder12.03.03

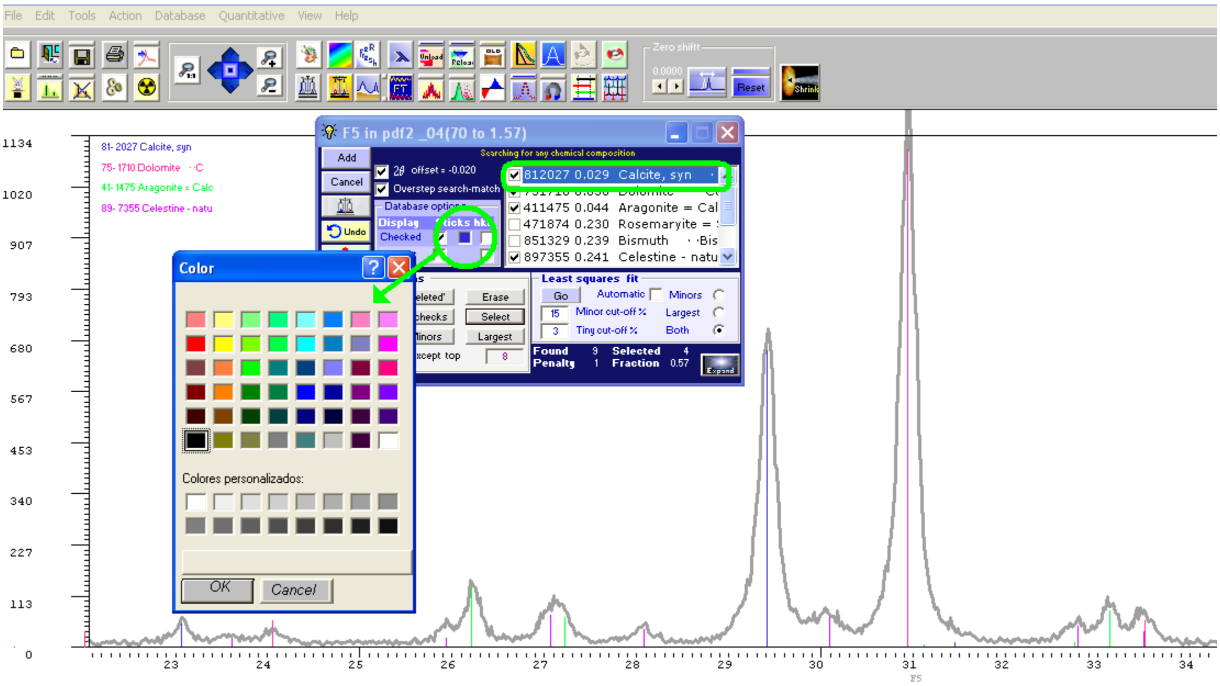
In version 03.03, direct reading of Bruker RAW patterns has been improved.

XPowder12

Ver XPowder12.03.04. CRITICAL UPDATE

1. The graphical matching between intensities of the experimental XRD patterns with those shown in some databases has been improved. Previously appeared some errors of the intensity scale due to that the 2θ scan interval in experimental diffractograms not includes the database maximum intensity, as occasionally happens at high 2θ angles.

2. The colors of the plots representing diffractogram patterns of databases can now be modified with the help of the tool as shown in Figure, where the change in color of the calcite database is illustrated. You can only change the colors of the checked phases.



Excluding elements from the periodic table in the search-match.

Very often happen incorrect determinations of crystalline phases, because with those with frequent chemical compositions appear a large number of phases with unusual compositions, but whose number is very large within the content of the databases. The problem is aggravated when the structures allow solid solutions, or when the number of phases is large.

A partial solution to this problem is to remove those elements which are not expected in the sample composition from the periodic table. This possibility has been introduced in the program, using a **tool** which is accessible using the button '**Periodic Table Edition Mode**' (Fig E1).

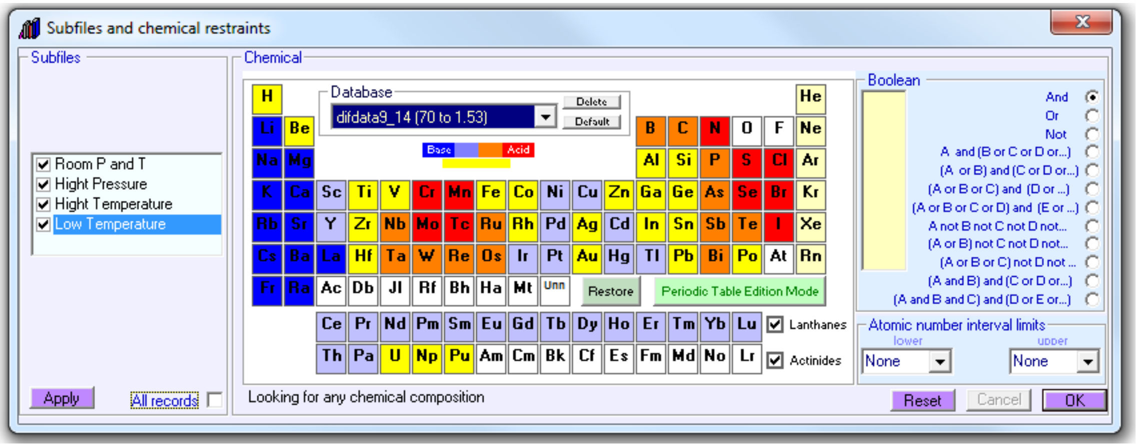


Fig E1. By clicking the '**Periodic Table Edition Mode**' button, you access the tool of Fig E2.

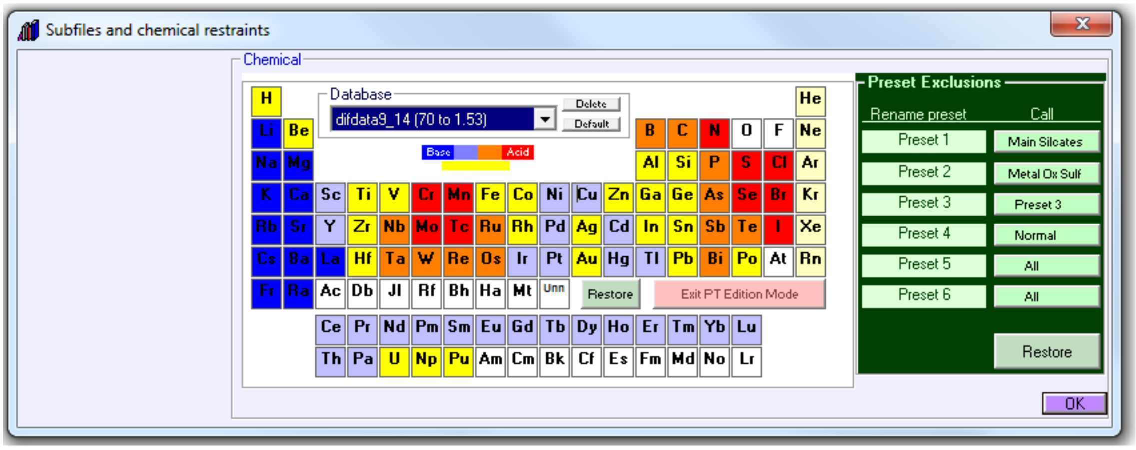


Fig E2. Individual elements can be ruled out (by clicking on the box the item as in Figure E3) or sequentially clustered (Figure E4).

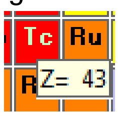


Fig E3. When it is Click on in the box of an item, it is discarded and then its symbol is written in white as Tc (Z=43) in picture.

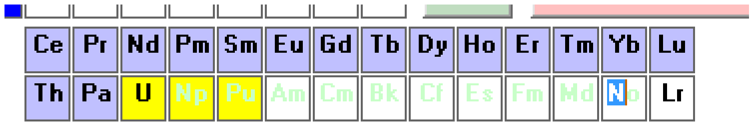


Fig E4. Pressing the shift key, clicking the first ('Np', Z= 93 in the picture) and last ('No', Z= 102 in picture), and finally releasing the shift key, the intermediate elements ($93 \leq Z \leq 102$) are discarded .

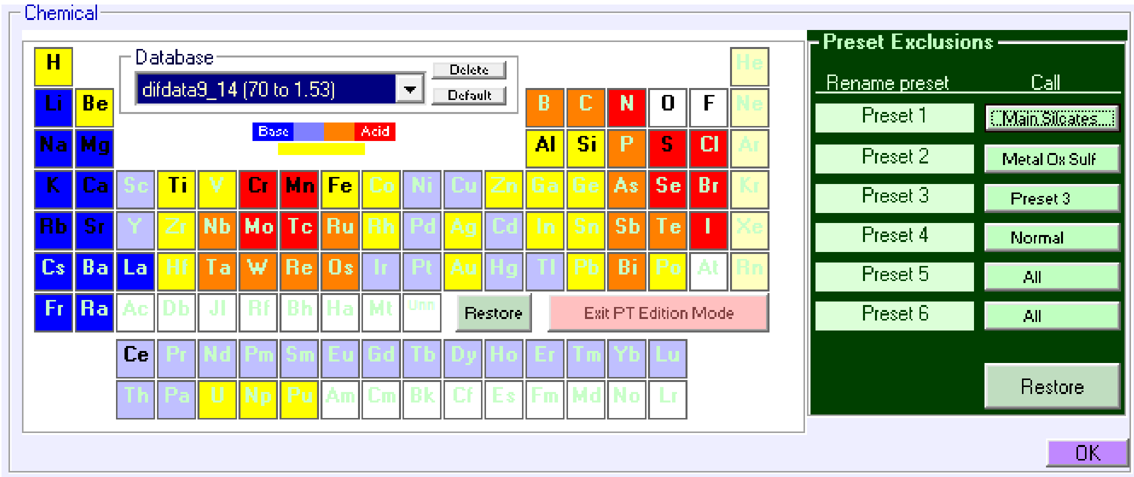


Fig E5. Also possible to use custom groupings presets. To do this just click on any of the buttons beneath the header 'Call'.

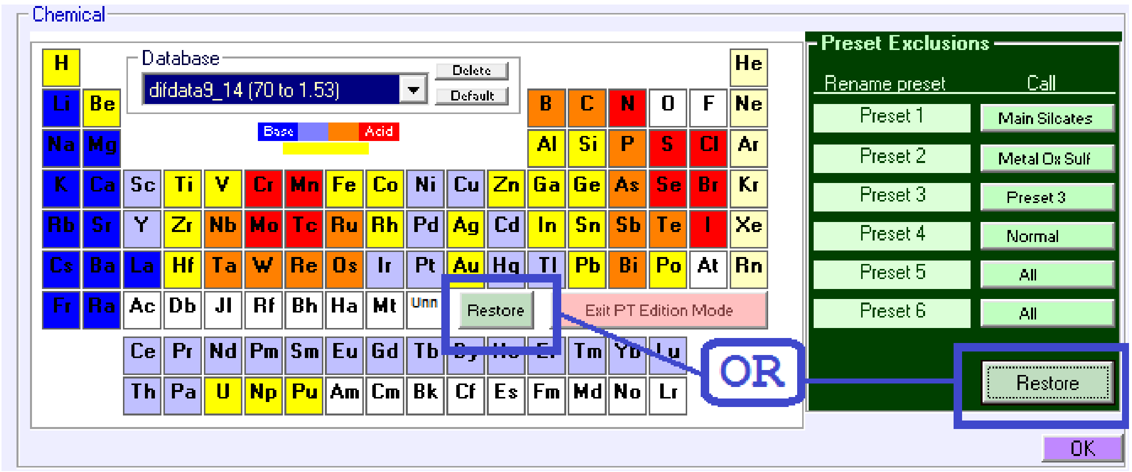


Fig E6. Any 'Restore' buttons reset all elements of the periodic table.

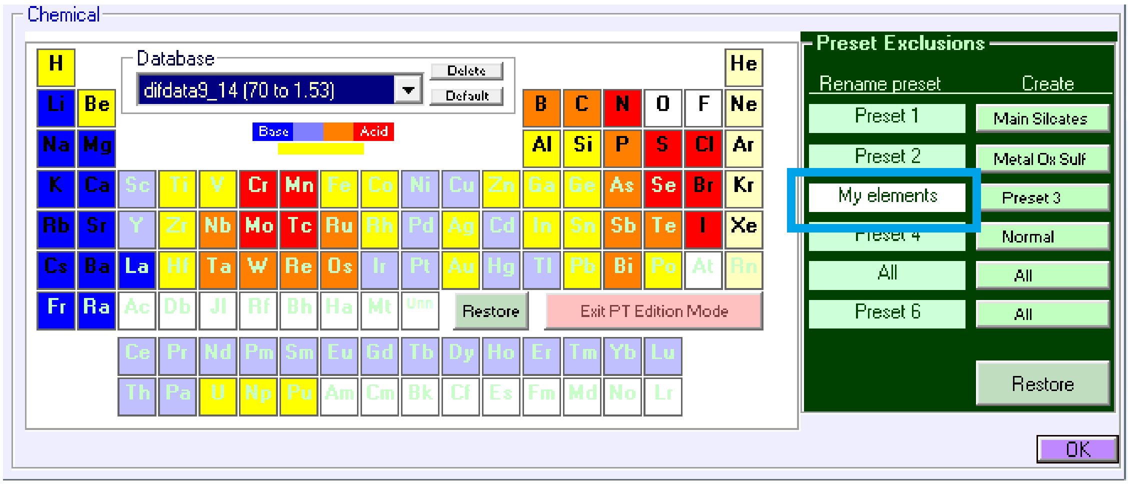


Fig E7. After exclusion of undesired elements, you can save your settings by clicking on any text box beneath the header 'Rename preset'.

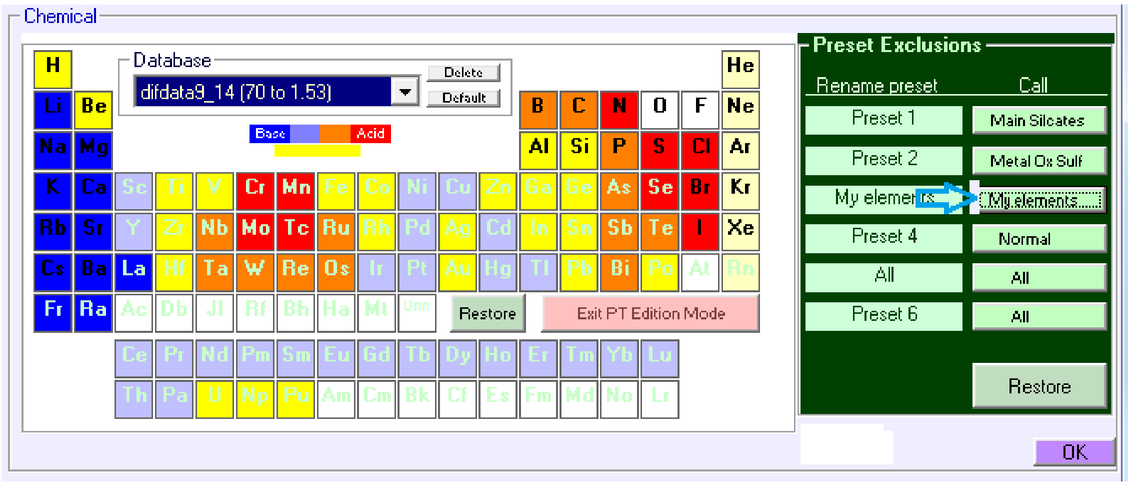


Fig E8. A double click on the text box, or simply click on the button ('My elements' in the example), save the preset.

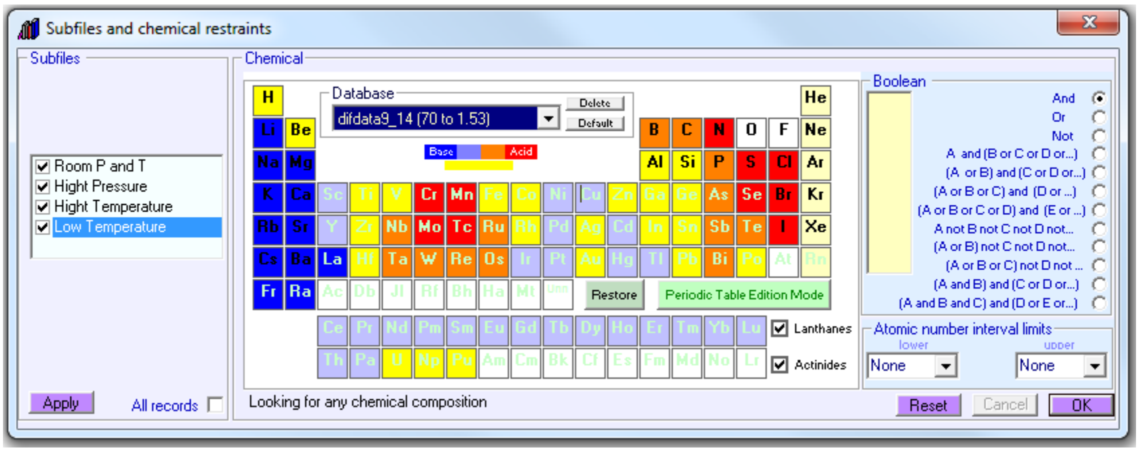


Fig E9. A click on the '**Exit PT Edition Mode**' button in Fig E8, leaves the 'edit mode' of the periodic system. Boolean operations can now be used on the remaining elements only. **Discarded *Elements* are recorded in the "Elements.Log" file and *Presets* in the "Preset.Log" file. Both files are charged by the program every time it reboots and does not change unless you delete them manually, or are edited again with the tools shown above.**

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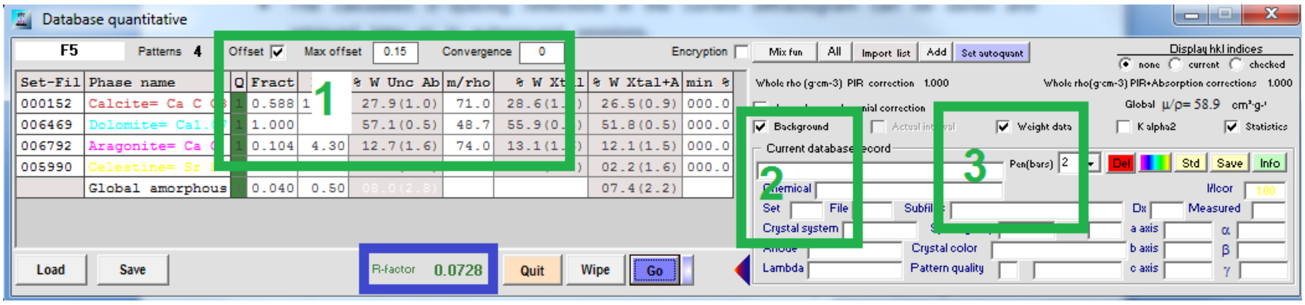
Ver XPowder12.04.35. CRITICAL UPDATE

- The calculated d-spacing reflections in the current diffractogram can be saved and retrieved later or in subsequent sessions.

  From the main menu use *File/ Preserve (Recover) d-spacings*.

- It has been rewritten completely the LS and SA routines for quantitative using database records based analysis. This does not change the results obtained in previous XPowder12 versions, but the appropriate values of R-factor will now get almost automatically. The calculation parameters that can be modified now are 2θ zero shift correction (**1**), virtual background subtraction correction (**2**) and statistical weighing experimental counts (**3**). It has removed the option of tuning of d-spacing database records because misuse of this option may cause mathematical artifice erroneous results, even even when R-factor values are low.



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